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"Intensity Ratios in a D. C. Spark

Using an Electro-Optical Shutter"

by

S. A. Heiberg, B.Sc. Fall 1950.

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INTRODUCTION

Spectroscopic study offers a quick method of quantitative chemical analysis requiring only very small samples. Calculations of percentage composition are based on working curves derived from samples of known composition. They depend on the determination of the relative intensities of appropriate spectral lines as emitted by a source containing the sample to be analyzed. Errors are often introduced by the presence of small amounts of some extraneous element which may produce a marked effect on the intensities of the lines from the element whose concentration is being studied. (1, 2, 3, 12, 13) This influence on line intensity may be either positive or negative. Even if the presence of the extraneous element is known it greatly complicates the problem of quantitative analysis.

To determine the factors that must be carefully controlled to minimize the effects of extraneous elements it is essential to learn more about the basic phenomena occurring in a spark discharge. The effects cannot be explained solely on the basis of a change in the effective discharge temperature since the temperature change required to produce the observed change in one pair of lines

does not always produce the observed change in another pair. (12) This apparent disagreement may be due to the measuring of time and space integrated radiation and may not constitute a refutation of the effective temperature concept. No correlation has been found between the magnitude of the intensity ratio variations and the atomic weight ratios or the ionization potential ratios, though in most cases some advantage is to be gained by using lines of nearly the same excitation potential. (13)

Work done by Brode, Langstroth, Newbound, Andrychuk and others on this problem has involved the integrated effects of many complete sparks. These effects are what are of importance in quantitative spectral analysis since an AC spark is generally used, but in order to study their causes it is necessary to study each stage of the spark separately. There is, for instance, a distinct difference between conditions during the first half of an oscillation when the current is going from the point to the plane and the second half when the current is in the opposite direction. Only one of the electrodes is loaded and the difference in shape produces an asymmetrical field. There may also be a difference in release conditions from spark to spark due to changes in the surfaces of

the electrodes. A single spark would not supply enough intensity for spectrographic work. Hence the conditions must be made as uniform as possible by ensuring that each spark strikes from a fresh surface of the loaded electrode and that the load is uniform.

Langstroth and Mayhood pointed the way in this attack on the problem, using stigmatic lighting of the spectrograph slit through a Kerr cell shutter to enable them to study the radiation from different points in the spark for the first 3, 6, or 9 half oscillations of the spark.

This work is concerned with an attempt to gain additional information by further breaking down the problem. Spectrograms were taken of the total radiation from 600-800 sparks using in turn the first 1, 2, 3, 4, 5, and 6 half oscillations plus the complete spark. The spectrograph slit was stigmatically illuminated to permit a limited study of the axial variations in intensity. Characteristics of the radiation from the later oscillations of each spark are largely masked by the inclusion of the radiation from all the preceding light pulses from that spark. This is unavoidable with the open-to-closed operation of the shutter as used in this work. Inaccuracy of measurement and the inability to measure absolute intensities

or to obtain exactly the same illumination on each exposure precludes the possibility of subtracting intensities of the first half oscillation from those of two half oscillations to obtain the intensities emitted during the second half oscillation alone. With recently developed high-voltage thyratrons (16) for charging and discharging the shutter it should be possible to obtain closed-to-open-to-closed operation of the shutter, particularly if a suitable cell liquid could be found that had a Kerr constant larger than that of chloroform. This would permit a much more detailed study than that attempted in this project.

APPARATUS

To avoid integrating the radiation from the total duration of the spark, a fast acting and accurately synchronized shutter is required. A Kerr cell, electro-optical shutter provides this fast action, being capable of closing in times of the order of 10^{-8} seconds. (8) Synchronization and delay control were obtained by the use of a modified Eccles-Jordan trigger circuit. The current through the source spark fed a signal to the trigger circuit. This gave an output pulse at the desired time interval after receipt of the input signal. After amplification, this pulse caused breakdown of a three-electrode spark gap, (see plate IV) which discharged and closed the shutter. The three-electrode gap proved to be a simple and reliable method of triggering the high-voltage discharge required to cause rapid closing of the shutter.

The Kerr Cell (6)

The cell was constructed of a piece of Pyrex tubing of 2.5 cm. inside diameter, 12.3 cm. long. The ends were ground plane. The windows, of fused quartz selected for freedom from strain patterns, were sealed to the ends of the cell with Sheffield's China cement. This cement was

not entirely satisfactory as it had a tendency to shrink and crack, producing leaks in the cell so that it required frequent refilling to avoid bubbles. From time to time it had to be taken apart and entirely recemented. However it was the best cement of several that were tested for their sealing properties and effects on the resistivity of the chloroform.

The plates of the cell were of 1/16" brass, 12.0 cm. long and 2.0 cm. wide with the edges rounded off. They were held accurately parallel by four small glass spacers cemented to the edges of the plates with china cement. These spacers also held the plates in position in the cell by bearing against the inside surface of the Pyrex tube. The electrical leads were of copper wire attached to the centre of the plates and passing out through sidearms sealed into the tube. These arms were sealed with china cement. A vertical arm was provided for filling the cell. A small bulb was blown in this tube to act as a reservoir and reduce the number of times that the cell had to be refilled due to the leakage that was never entirely eliminated.

Chloroform was chosen as the cell liquid since it is transparent to wavelengths in the ultra-violet region

most of the persistent lines used in spectral analysis lying between 2500 A and 4000 A. The relatively low Kerr constant of chloroform necessitated the use of very high voltages to produce even partial transmission. Twenty kilovolts was supplied from a resistance capacitance filtered, half-wave rectifier. At this high voltage the resistivity of the chloroform was required to be very high to restrict the current through the cell which would cause distortion of the image. The chloroform was distilled twice, the vapor passing through calcium chloride to remove water. The first ten percent was discarded each time as well as anything left after the temperature reached sixty degrees centigrade. The third time it was distilled directly into the cell. The cell had been rinsed with dilute nitric acid and with distilled water and dried. It was allowed to stand overnight with the chloroform which was then discarded and the cell refilled as before. There was then a resistance of the order of 1,000 to 2,000 megohms between the plates as measured by the leakage of charge from a one microfarad condenser using an electrostatic voltmeter. This resistance was very variable, generally rising several hundred megohms after a high potential had been applied for 15 minutes, due to the clearing away of the ions by the process referred to by

Möller as "selbstreinigung". (17) With these precautions no distortion was evident under a field of forty kilovolts per cm.

The Electro-optical Shutter

The cell was placed between crossed Foucault prisms oriented with their axes at forty five degrees to the field direction. (see plate III) The applied voltage being insufficient to produce a phase difference of 180 degrees between the two components of the light, the polarized incident beam emerges elliptically polarized. The transmission of the cell is then given by:

$$I = I_0 \sin^2 (\pi BLE^2) \quad (4, 5,)$$

where:

I_0 is the intensity entering the cell

I is the intensity passing the analyzer

B is the Kerr constant of the cell liquid in
 $\text{sec}^{-2} \text{ cm}^{-1}$

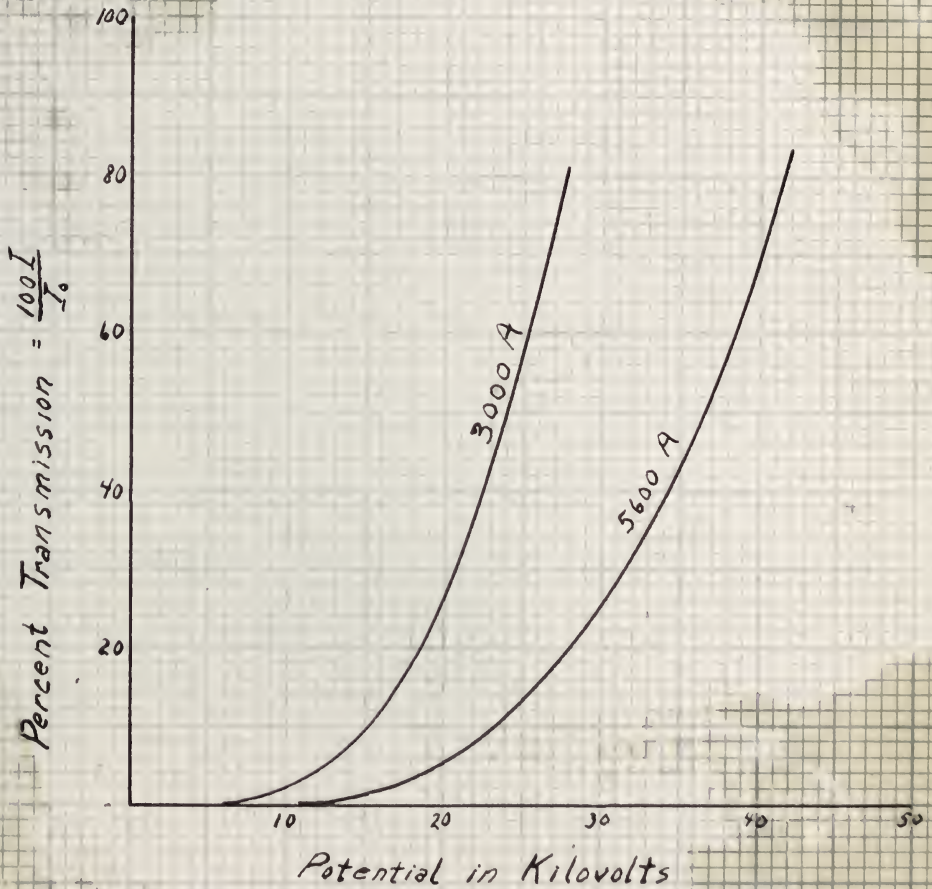
L is the length of the cell in cm.

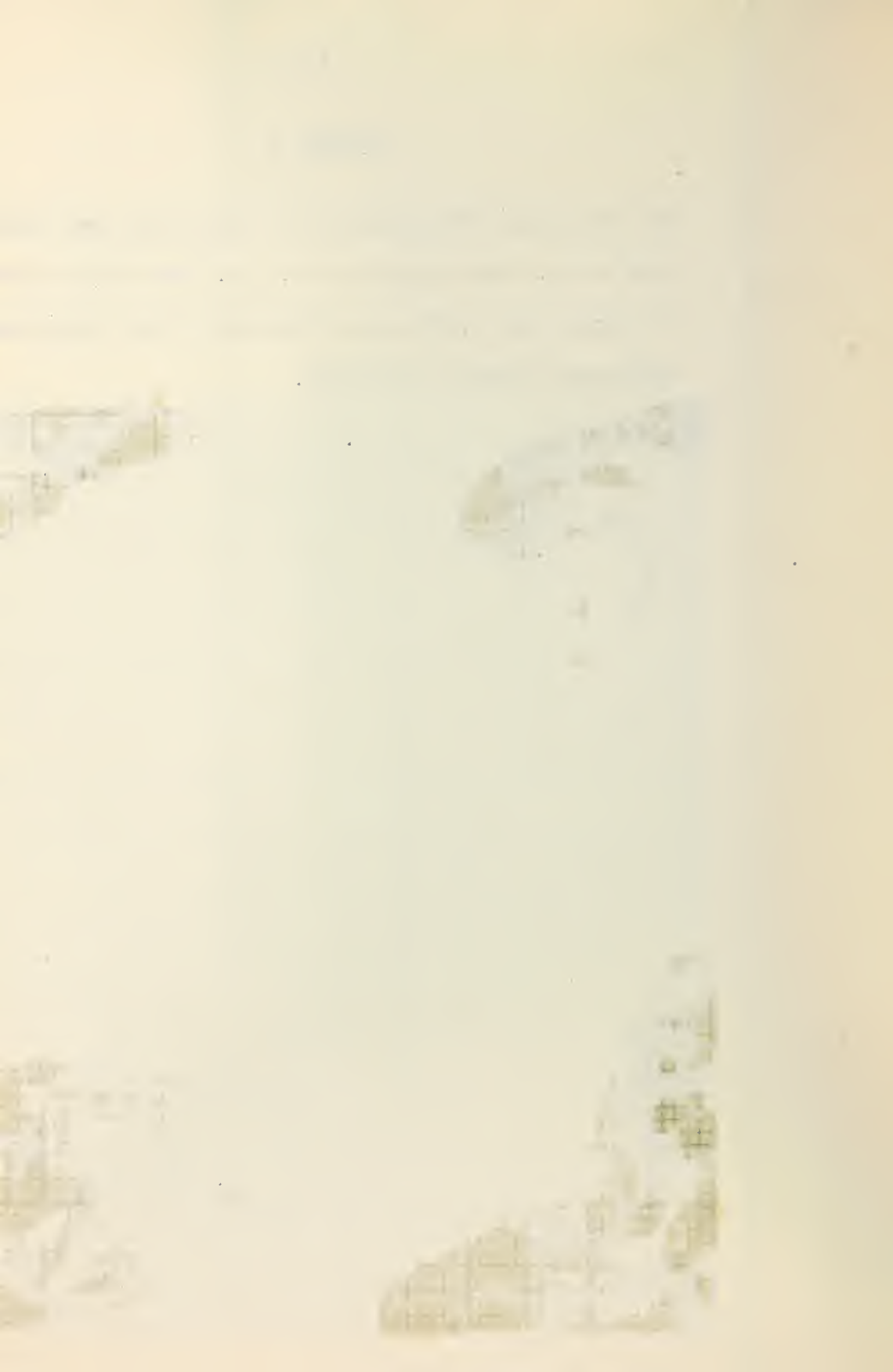
E is the applied electric field in statvolts per cm.

Figure 1. page 9 shows a graph of the percent transmission of a cell of the dimensions specified above, at 3000 Å and at 5600 Å, plotted as a function of the potential

FIGURE 1

The Calculated Transmission of a Chloroform Kerr Cell with 12 cm. Plate Length and 0.5 cm. Plate Separation, at 3,000 A and 5,600 A as a Function of the Potential Difference between the Plates.



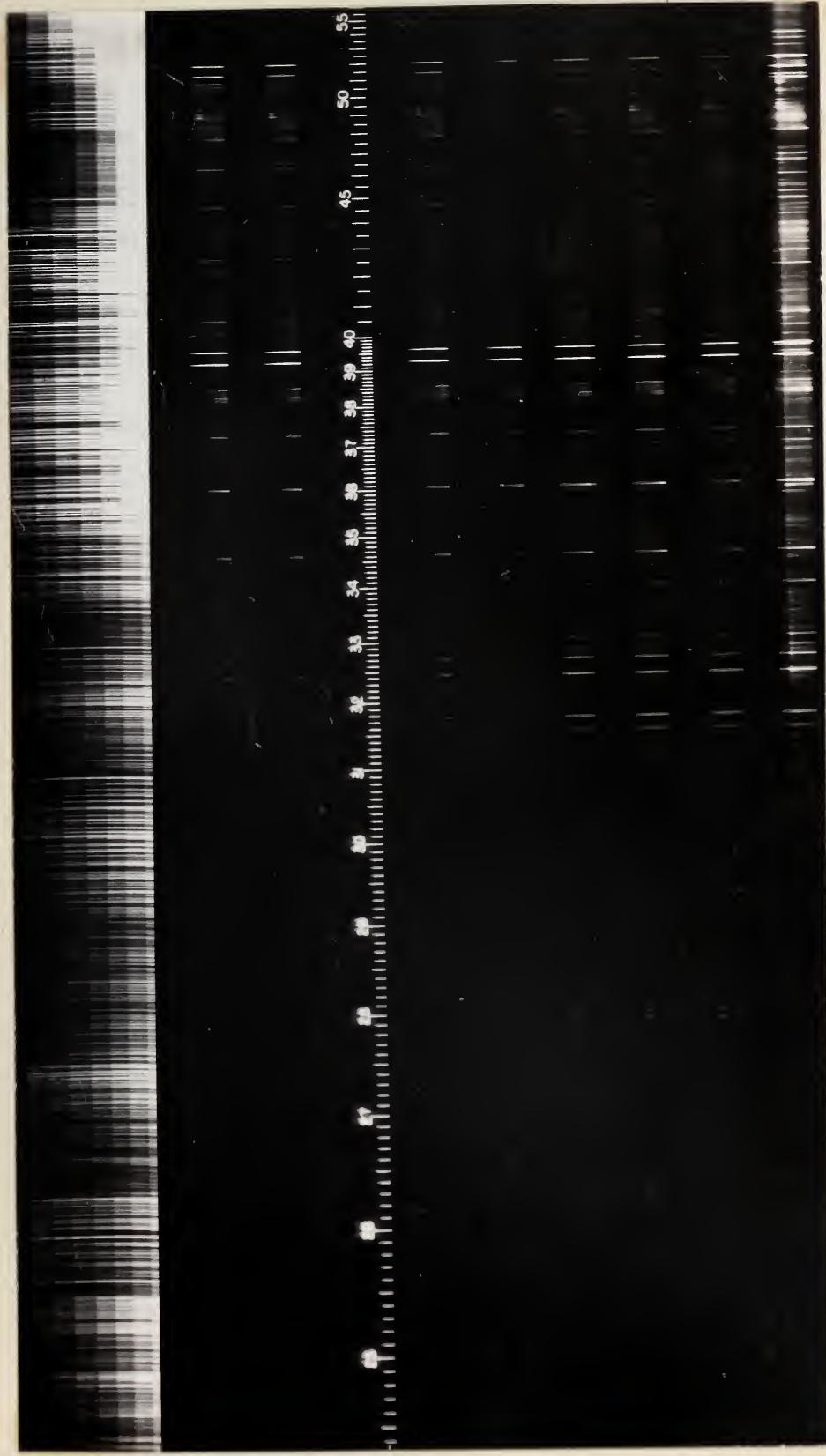


difference between the plates. Kerr constants of -8.40 and -3.53 respectively, were used for the computations. (5, 9) As shown by the graph, a potential difference of twenty kilovolts applied to the plates will give a transmission of approximately 27% at 3000 A.

The spark source was placed at the focus of a quartz collimating lens of 25 cm. focal length. The image of the electrodes was focussed on the spectrograph slit by a quartz lens of 15 cm. focal length giving a magnification of $3/5$.

Performance of the Foucault Prisms

The chloroform of the Kerr cell will transmit wavelengths as low as 2500 A. The lower limit of radiation passed by the shutter is determined by the Foucault prisms. In order that the O ray shall be totally reflected at wavelengths up to 4450 A the angle of incidence at the air space in the prism must be more than $36^{\circ} 41'$. To pass the E ray at 3000 A it must be ~~more~~^{less} than $40^{\circ} 39'$. This leaves a range for the angle of incidence of the order of four degrees. The practical range is smaller yet since the internal reflection is very high for angles within one degree of the critical angle and the external reflection in the air gap is high within two or three

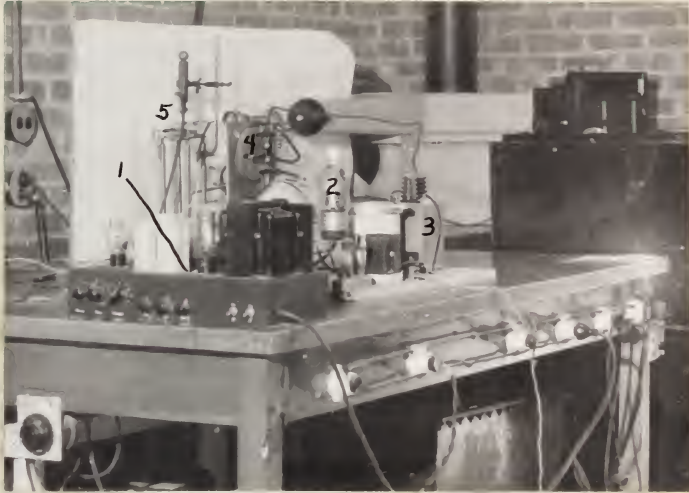


Print of a spectrographic plate showing the cut-off progressing downward from 3800 Å due to total reflection of both the O and E rays in the Foucault prism



degrees of the critical angle. With a 4 mm. spark placed 25 cm. from the collimator there was a divergence of one degree between rays from opposite ends of the spark. This resulted in the elimination of light from near the plane electrode below 3150 Å, the lines getting progressively shorter until they disappear at about 2700 Å. When the analyzer was turned through 180 degrees the other end of the spark was cut off as well, below 3600 Å. Accordingly care was taken to keep the Foucaults so oriented that they both cut off the same end of the spark. The parts of the lines that appeared in this region could be measured and the ratio of the intensities of two lines would not be affected as long as they were close enough together to have been reduced in intensity by an equal amount. However the ratio of the exposures of two points along the same line would not be representative of the relative intensities of that wavelength emitted from the corresponding points in the spark. In order to study lines in the range below 3200 Å the prisms must be set accurately at an angle to the axis of the shutter that will give maximum transmission in this region, perhaps at the expense of attaining complete closing of the shutter for higher wavelengths.

PLATE I



1. Time Control Unit

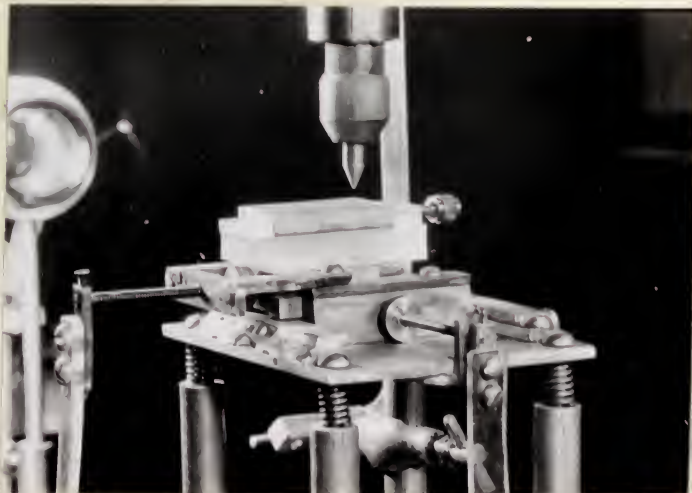
3. Pulse Transformer

2. Hydrogen Thyatron

4. Three-electrode Gap

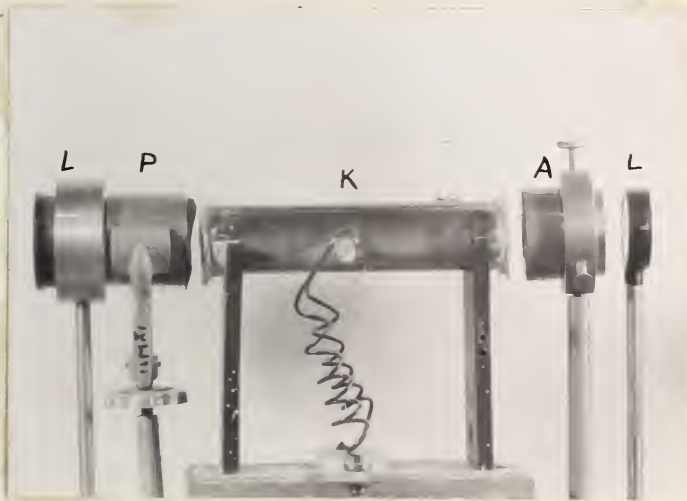
5. Source spark unit

PLATE II



Source Electrodes and Carrier

PLATE III



Electro-Optical Shutter

L L Lenses

P Polarizer

K Kerr Cell

A Analyzer

PLATE IV



Three-Electrode Spark Gap

Synchronization and Delay Control

The control circuits were as shown in figure 4. The spark current passing through the coil L_1 induced a pulse in the tickler coil which tripped the 884 thyatron. The thyatron served to amplify the pulse and also isolated the trigger circuit from the effects of subsequent oscillations in the spark current. The pulse stopped the current in the first 6AC7 pentode which was normally conducting, causing the other to fire. The rise in the anode potential of the second pentode on the re-exchange of current tripped the amplifying 884 thyatron and subsequently a high-voltage hydrogen pulse thyatron. This pulse, further amplified by a 4:1 pulse transformer was applied to the auxiliary electrode in the three-electrode spark gap providing much more than the minimum breakdown potential for the space between it and the grounded sphere.

The two main electrodes of the three-electrode gap (see plate IV) were nickel-coated brass spheres 2 cm. in diameter, 1.4 cm. apart, connected in parallel with the Kerr cell and with a 0.0025 microfarad condenser. The third electrode was a pointed brass rod with the point bent toward the grounded sphere. The gap between the point and sphere was 3.5 mm.

Figure 2 Spark Source Circuit

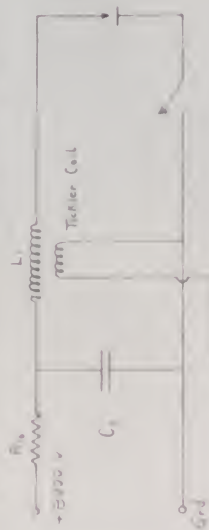


Figure 3. Kerr Cell Circuit

Calibration

The capacitance of 0.4 microfarads and the inductance of 350 microhenries in series with the source spark gave an oscillation frequency of 13,000 per second. To determine the time at which the shutter closed relative to the time of the initial breakdown, the light from the spark was passed through the shutter, reflected off a rotating mirror and focussed on a strip of 35 mm. Linagraph Ortho film. The successive light pulses from each half oscillation of the spark were spread over the film so that the number passing through could be determined. (see plate V below)

PLATE V

1
1/2 Half Oscillation

2 " "

3 " "

4 " "

5 " "

6 " "

A concave spherical mirror of 25 cm. focal length was placed on the side of the spark opposite to the shutter with the gap at its focus to increase the amount of light falling on the film. About one spark in four showed up on the film. The delay was varied by changing R_T and C_T in the trigger circuit. The right settings to pass 1, 2, 3, 4, 5, or six half oscillations or the whole spark were determined roughly by the use of an oscilloscope. For this a signal from the source spark current was fed to the horizontal plates and the output pulse of the delay unit to the vertical plates. A more accurate determination was then made photographically using the rotating mirror. In order to obtain closing after the first half oscillation it was necessary to reduce the bias on the input 884 thyatron to a value that made it fire occasionally due to stray signals. For any given settings no variation was observed in the time of closing of the shutter. It is estimated that the amount of light admitted at any setting of the controls did not differ from that of the whole number of half oscillations desired by more than ten percent of the total light emitted by the last half oscillation.

The Source Spark Unit

In order that the electrode load might not be used up it was necessary that each spark should strike from a fresh surface. The condenser in parallel with the source spark gap was charged through a water resistor so that the switch could be opened after every spark. This made it possible to move the plane electrode over after every spark so that the next would strike from a fresh surface. The electrode carrier was made to slide longitudinally or laterally, movement being by means of two 6-32 screws at right angles to each other. (see plate II) Thus the sparks traced parallel paths back and forth across the electrode with each spark $1/32$ inch from the next. The plane electrodes were made of $1/4$ inch copper sheet cut in pieces about 2 cm. by 3 cm. One side was ground plane and smooth. The point electrode was a $1/4$ inch copper rod machined to a forty five degree point.

The Spectrograph

A Hilger medium quartz spectrograph was used.

EXPERIMENTAL PROCEDURE

The solution used as a standard sample for loading the electrodes contained magnesium chloride, calcium chloride and cadmium chloride. The concentration was such as to give approximately 10^{17} atoms per cm^2 of magnesium and calcium and four times as many of cadmium when 0.05 cc. of the solution were applied per square centimeter of the electrode. The greater amount of the latter was used because it was found that the cadmium lines showed up only very faintly if the cadmium were introduced in the same concentration as the others. The most intense lines of cadmium are below 2500 A or above 5000 A. Stannous chloride was then added as an extraneous element in the same proportion as the magnesium and the calcium. This solution had to be prepared immediately before loading the electrodes as the tin soon began to precipitate out as stannous hydroxide. In a third sample boric acid was added as an extraneous material.

Table I shows the composition of the samples giving the atomic weights and the first ionization potentials of the elements introduced and the weight of each per cm^2 of the deposit.

TABLE I COMPOSITION OF SAMPLES

Element	Atomic Mass (Mass Units)	First Ionization Potential	Salt Form Introduced	Micrograms Salt per cm ² on Electrode
Standard Sample (Load 1)				
Mg	24.3	7.6 v.	MgCl ₂ ·6H ₂ O	33.6
Ca	40.1	6.1 v.	CaCl ₂	18.4
Cd 112.4	112.4	9.0 v.	CdCl ₂ ·2 1/2H ₂ O	121.6
Std. Sample + SnCl ₂ (Load 2)	118.7	7.3 v.	SnCl ₂ ·2H ₂ O	37.5
Std. Sample + H ₃ BO ₃ (Load 3)	10.8	8.3	H ₃ BO ₃	28.5

Preparation of the Electrodes

The electrodes were ground plane and polished on one side. They were then cleaned in nitric acid, washed in running water, rinsed in distilled water, and dried. The load was applied with a 0.05 cc. pipette with 0.05 cc. of solution per square centimeter of the electrode. The solution would not spread over the entire surface without the addition of more distilled water. This produced a heavier ring of salt around the edge when the water evaporated. Better results were obtained by adding a minute amount of aerosol to the solution after application to the electrode. This reduced the surface tension and allowed the solution to spread evenly over the surface. The electrodes were dried under reduced pressure. Rapid drying seemed to be conducive to the formation of a uniform deposit. More electrodes were prepared than were required so that the ones with the most uniform coating could be chosen for use. The ones containing boric acid were particularly difficult to coat evenly, the salt having a tendency to collect in small patches of greater thickness.

Exposure of the Plates

The point electrode was placed at the focus of the collimating lens of the shutter. A lamp was placed behind it and the shadow of the point was focussed on the slit of the spectrograph with the Foucaults uncrossed. The analyzer was then turned to cut-off. The slit width was set at 50 microns. A loaded plane electrode was placed in the carrier and the gap set at 4 mm. The gap length was checked with an accurately machined brass spacer at the four corners of the plane electrode to see that its surface was parallel to the plane of motion of the carrier and ensure that the gap would remain constant. For one exposure 600 sparks were allowed to pass, the delay being set to close the shutter after the desired number of half oscillations. When only one half oscillation was passed, 800 sparks were used per exposure to ensure that all the lines would appear with a measurable density. New plane and point electrodes were inserted for every exposure.

The voltage was set at 8,000 volts which was only slightly above minimum breakdown potential, as indicated by a noticeable interval between the time of closing the switch and the initiation of the discharge. Four to

five seconds were allowed between successive sparks to give the shutter time to open fully again. The plane electrode was moved $1/32$ inch after each discharge. Performance of the shutter was checked by the discharge in the sphere gap. This failed to operate only once in about one thousand sparks. The spectra radiated during 1, 2, 3, 4, 5, and 6 half oscillations and the whole spark, with the standard load on the plane electrode, were recorded on a 4"x10" Kodak super ortho-press plate. This was repeated using loads 2 and 3 containing additions of stannous chloride and boric acid respectively.

Intensity calibration marks were put on each plate with an iron arc and a logarithmic step sector. The arc was placed 97 cm. from the spectrograph slit and the sector immediately in front of the slit. The arc was run for one minute and forty-five seconds at 2.5 amperes DC with a gap of 3 mm.

Processing of the Plates

The plates were developed six minutes in D-19 developer, washed one minute in water, fixed thirty minutes in F-5 acid hardening fixer, washed one hour in running water and rinsed with distilled water. All solutions

were at twenty three degrees centigrade.

Measurement of Intensities

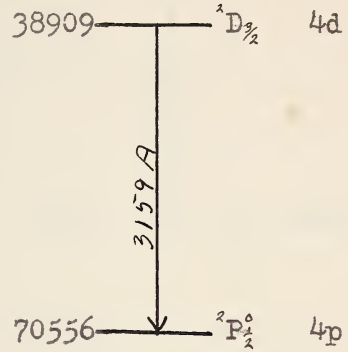
The densities of the lines studied were measured with a microdensitometer constructed at the university. It was given a twenty minute warm-up before use to allow the intensity of the lamp to become stabilized. Intensity calibration curves were drawn for several points along the range of wavelengths studied. Measurements were made at three points on each line corresponding to positions near each end and at the middle of the spark. The background was measured for each line.

The lines measured and the energy levels involved in the transitions giving rise to them are given in table II. Partial energy level diagrams are shown on pages 26 and 27.

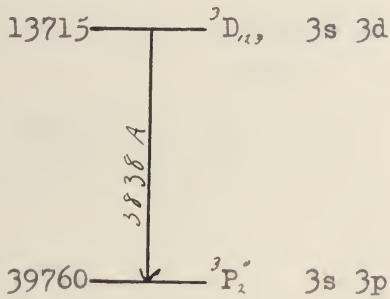
TABLE II

Lines Studied and the Energy Levels Involved

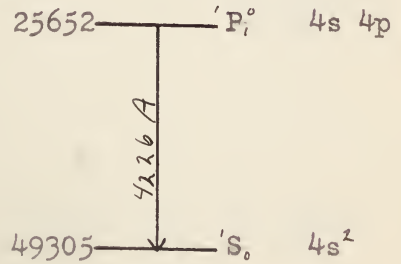
Element	Wavelength	Excitation Potential	Final Level	Initial Level
Ca II	3159 Ångströms	13.1 v.	$^2P_{\frac{1}{2}}^o$ 4p	70556-- $^2D_{\frac{3}{2}}$ 4d 38909
Sn	3175 "	4.3 v.	3P_2 5p6s	55764-- $^3P_1^o$ 5p ² 24277
Cd	3261 "	3.8 v.	1S_0 5s ²	72539-- $^3P_1^o$ 5s5p 41883
Sn II	3352 "	18.3 v.	$^2D_{\frac{5}{2}}$ 5s5p ²	59464-- $^4F_{\frac{7}{2}}$ 5s ² 5f 89288
Cd	3403 "	7.3 v.	$^3P_0^o$ 5s5p	42425-- 3D_1 5s5d 13052
Cu	3599 "	7.2 v.	$^2P_{\frac{3}{2}}^o$ 3d ⁴ 4p	31524-- $^2S_{\frac{1}{2}}$ 3d ⁴ 8s 3739
Cu	3602 "	7.8 v.	$^4D_{\frac{7}{2}}^o$ 3d ⁴ 4s4p	18794-- $^3d^4s(^3D_3)$ 4d -8960
Cd	3610 "	7.3 v.	$^3P_2^o$ 5s5p	40712-- 3D_3 5s5d 13023
Mg	3838 "	5.9 v.	$^3P_1^o$ 3s3p	39761-- $^3D_{1,2}$ 3s3d 13715
Ca	4226 "	2.9 v.	1S_0 4s ²	49305-- $^1P_1^o$ 4s4p 25652



———— Ionization
Level



———— Ionization
Level

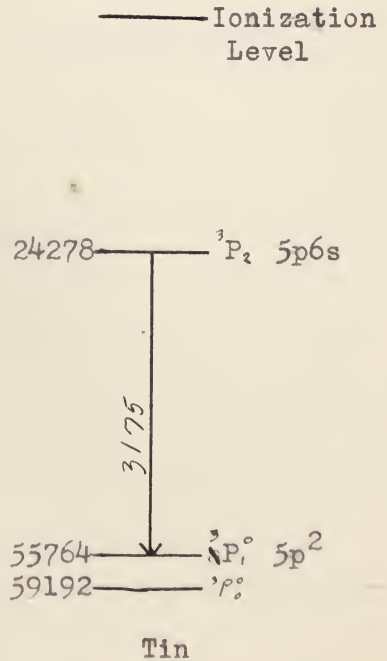
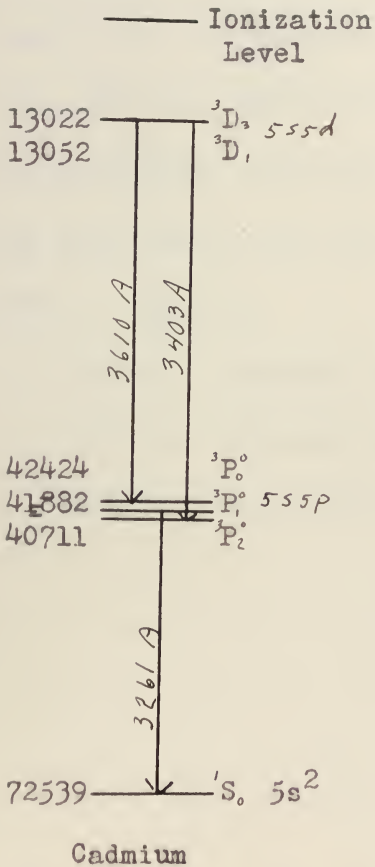
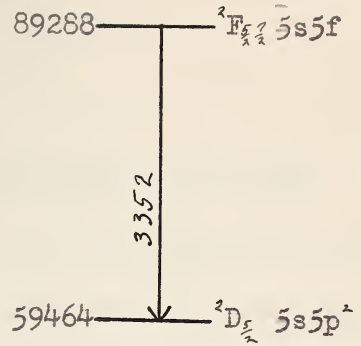


Magnesium

Calcium

Partial Energy Level Diagrams for Magnesium and Calcium

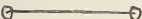


The column of numbers to the left of the diagrams indicates the wave-number corresponding to the energy level. Vertical lines indicate transitions giving rise to lines studied in these experiments.



Partial Energy Level Diagrams for Cadmium and Tin

RESULTS

The results are presented graphically in figures 5 to 14 inclusive. The ordinates give the ratios of the intensities of the pair of lines, measured at three points along the line as indicated by the following color code:

 near the plane electrode
 at the centre
 near the point electrode

The abscissae give the number of half periods of the spark that contributed light to the exposure. 'F' indicates that the shutter was open for the full duration of the discharge. The electrode coating used is given by the load number according to the designations given in table 1. page 20.

Load 1. Standard sample

Load 2. Stannous chloride addition

Load 3. Boric acid addition

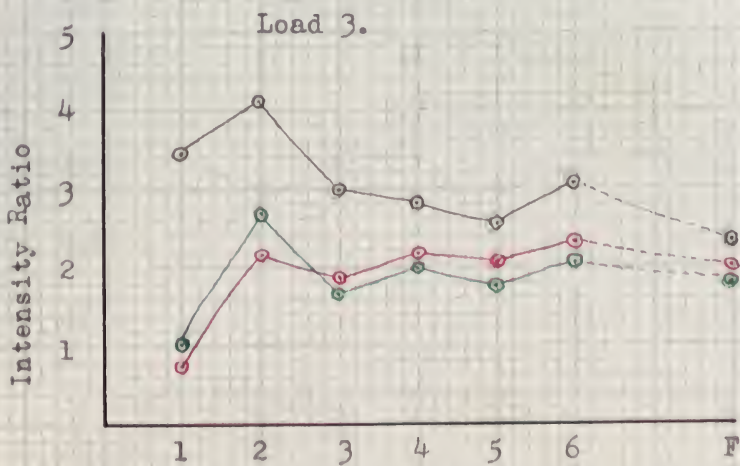
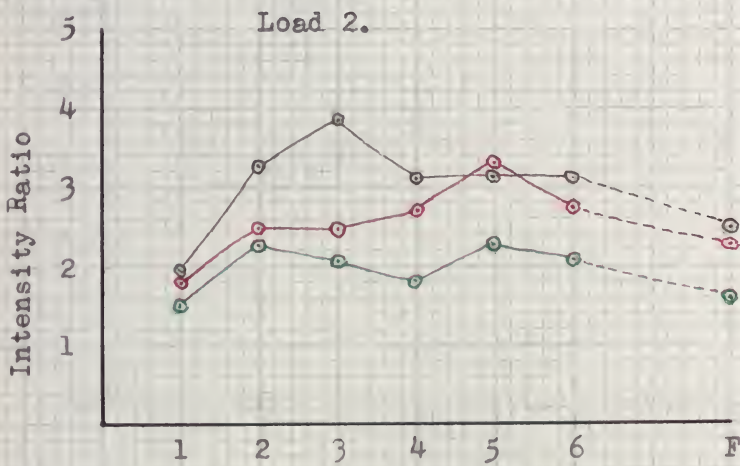
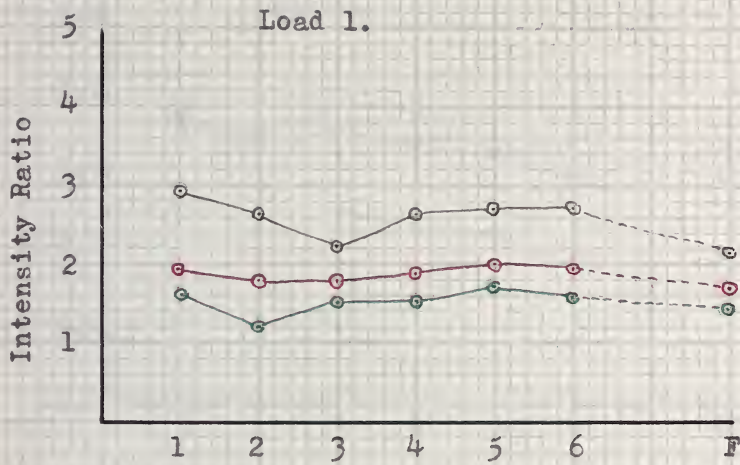
DISCUSSION

The accuracy of the intensity measurements was estimated to be of the order of 10%. This would make a 20% change in the ratios the least that could be considered significant. Accordingly more attention has been paid to general trends than to individual measurements.

Synchronization and delay control of the shutter were found to be reproducible when tested with the rotating mirror, and errors introduced by them would be small compared to other errors.

The shutter arrangement used was successful in cutting off the light at any desired point and permitted a study of intensity variations in a relative manner. Closed-to-open-to-closed operation of the shutter is essential if detailed information is to be obtained. For a more accurate study of the axial intensity distributions higher magnification of the image must be used. This requires the passage of many more sparks per exposure which necessitates an automatic arrangement for closing the switch and moving the electrode. Even an exposure of 600 sparks becomes very laborious under manual operation.

Figure 5. Ratio $\frac{\text{Mg3838}}{\text{Ca4226}}$



Exposure Time in Half Oscillations

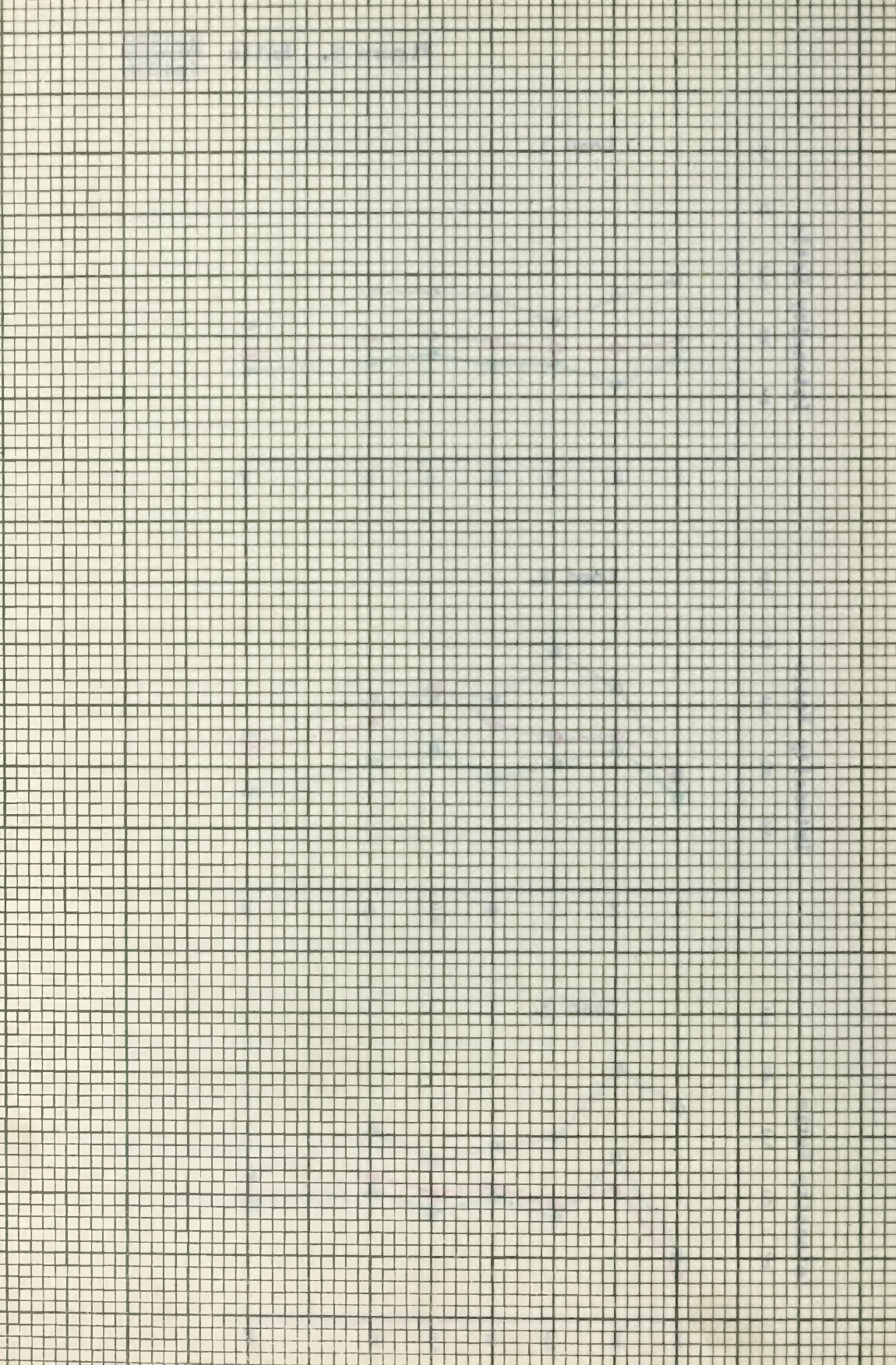
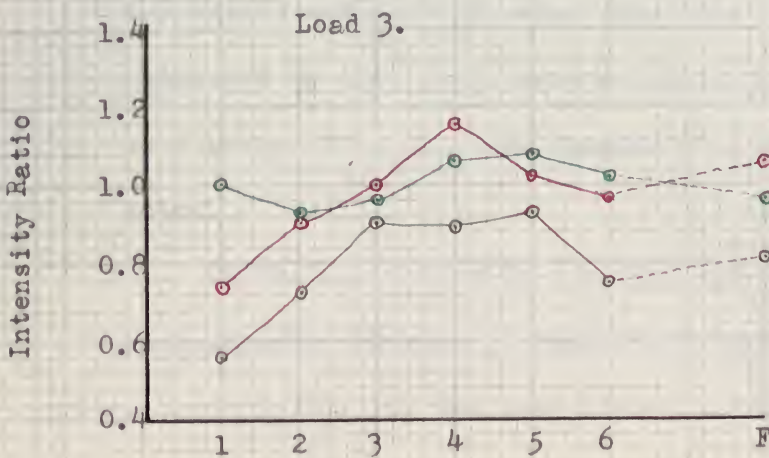
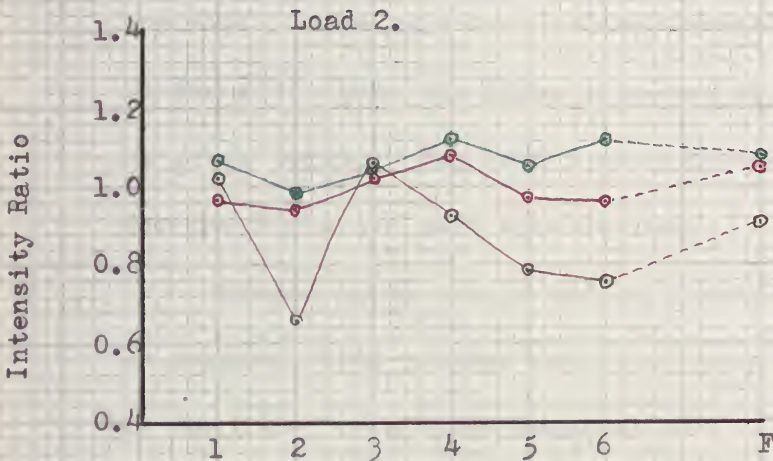
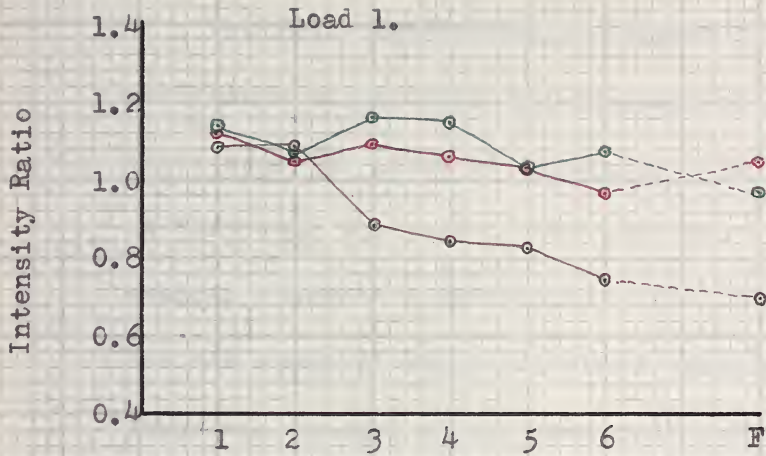
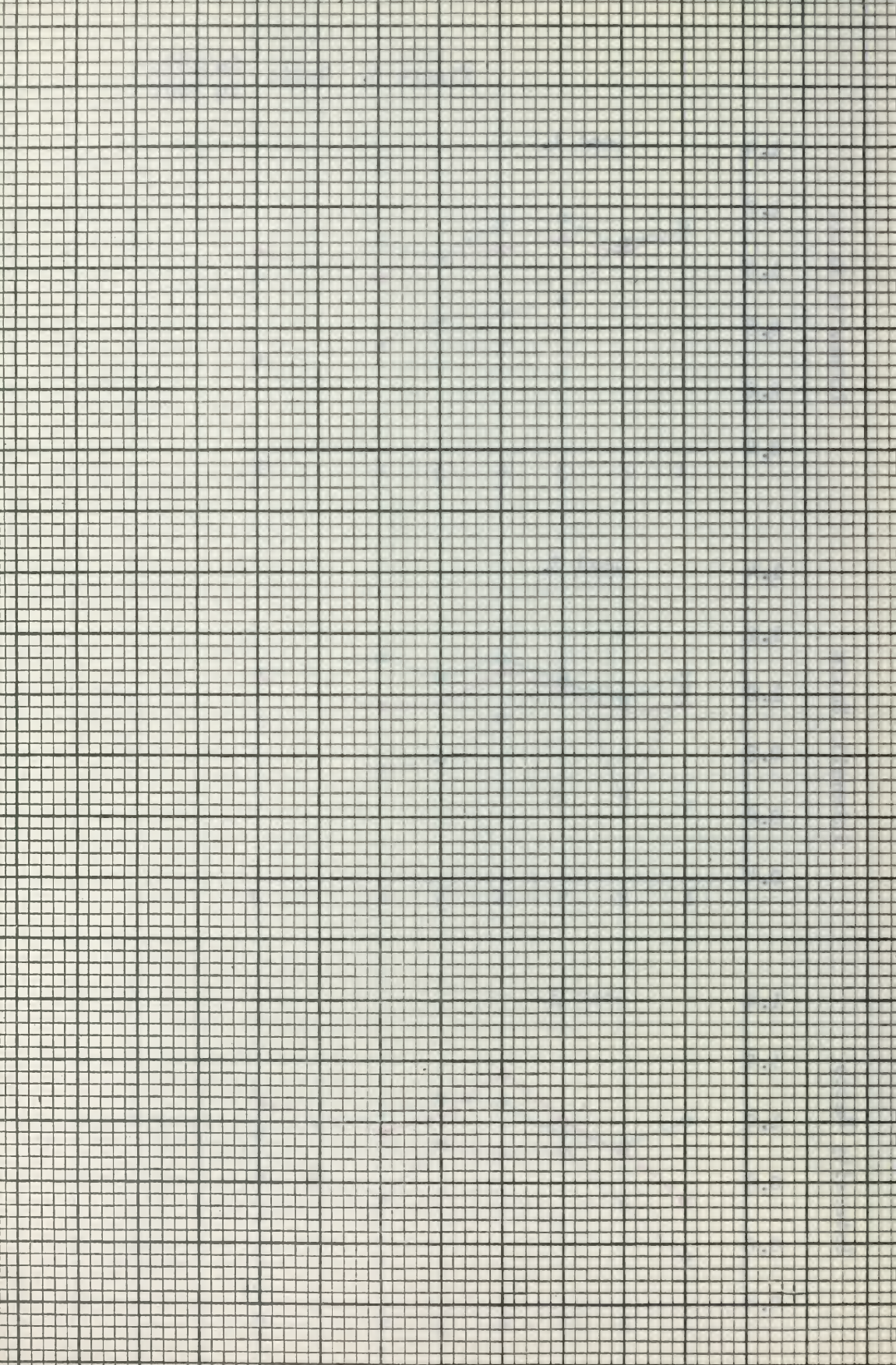


Figure 6. Ratio $\frac{\text{Cu3599}}{\text{Cu 3602}}$



Exposure Time in Half Oscillations



The ratio $\text{Mg}3838/\text{Ca}4226$ (Figure 5) shows very little percentage change over the duration of the spark. The value near the plane is generally $1\frac{1}{2}$ to 2 times as high as that near the point. The addition of extraneous substances produced a variation in the initial stages. For the standard sample the most uniform axial distribution was reached after three half oscillations. The initial distribution was very uniform for load 2 but through the first three half oscillations there was a marked increase in the ratio near the plane that was not so pronounced at other points. For load 3 this increase lasted only for the first two half oscillations.

Changes in the ratio $\text{Cu}3599/\text{Cu}3602$ (Figure 6) could be measured with greater precision than some of the others as the lines were close together and of nearly the same magnitude so that errors in calibration or background correction would be the same for both. Temperature changes indicated by this ratio were calculated using an assumed mean temperature of 7,000 degrees at the centre of the spark.

If the excitation in a source can be assumed to be predominantly thermal in character, the observed intensity ratio (I_i/I_n) of two transitions arising from different

energy levels of an atom or molecule, will be closely described by the relation:

$$I_i/I_n = P_{in} e^{-\Delta E_{in}/kT} \quad (10)$$

where:

P_{in} is a constant involving the wave numbers of the transitions, the transition probabilities, and the statistical weights of the initial levels.

E_{in} is the difference in energy between the initial levels of the two transitions.

k is Boltzmann's constant

T is the distribution modulus corresponding to the temperature of the vapor.

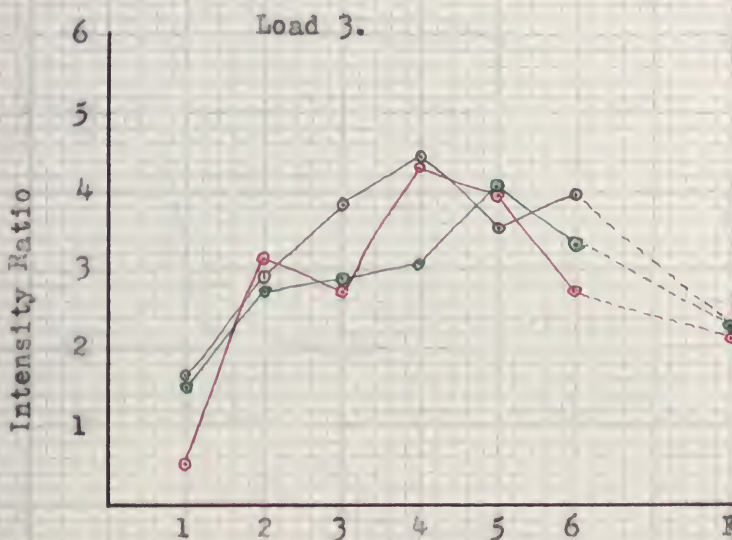
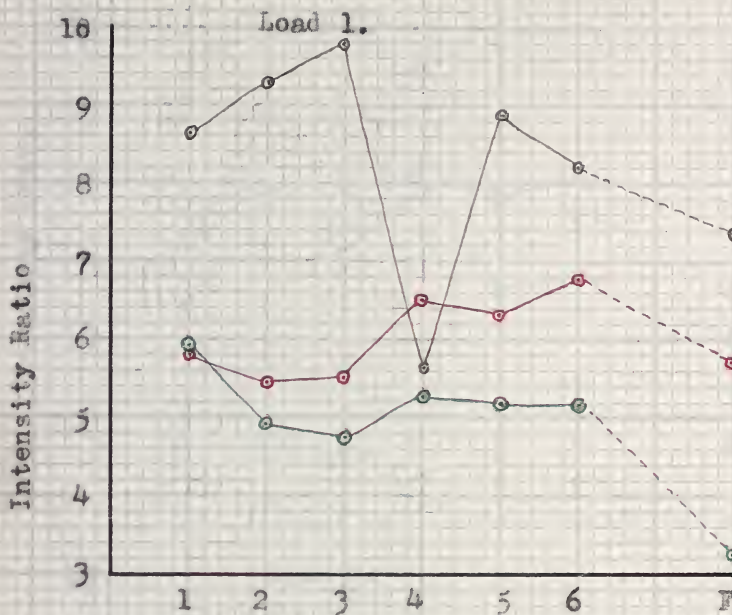
If an approximate value for T is assumed, a value for P_{in} may be determined that will give reasonably accurate values for the temperature variations when substituted in the equation:

$$\Delta T = \frac{k}{P_{in} E_{in} e^{-\Delta E_{in}/kT} T^2} \cdot \Delta (I_i/I_n)$$

which is derived by differentiating the equation above.

Maximum variations were of the order of 500 degrees. For load 1 there was a fairly steady drop in temperature over the duration of the spark. The addition of tin produced a drop in the ratio for the second half oscillation

Figure 7. Ratio $\frac{\text{Cd3403}}{\text{Cd3261}}$



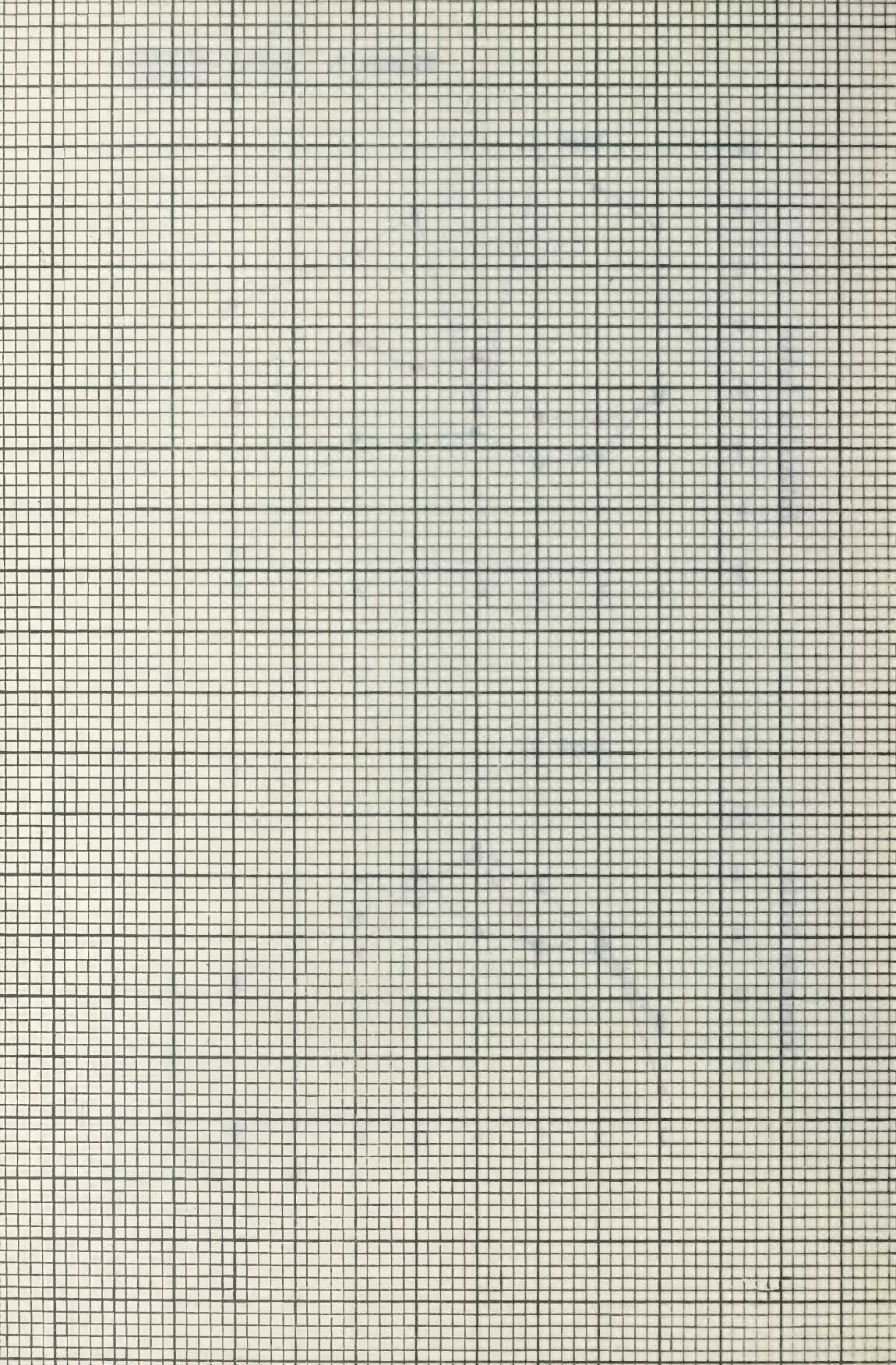
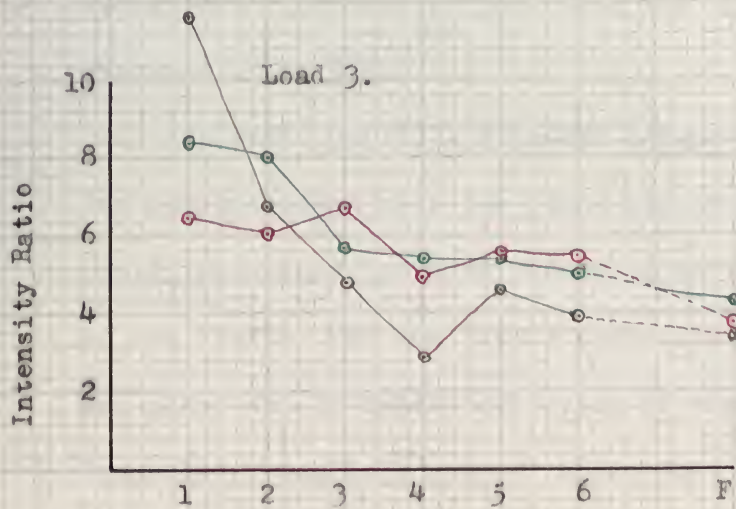
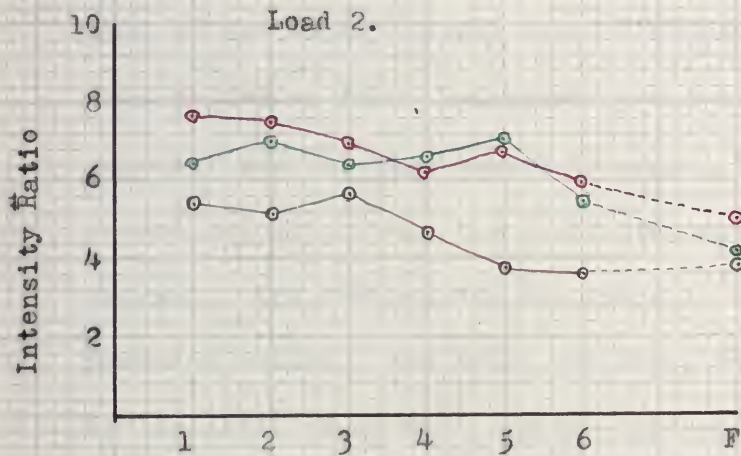
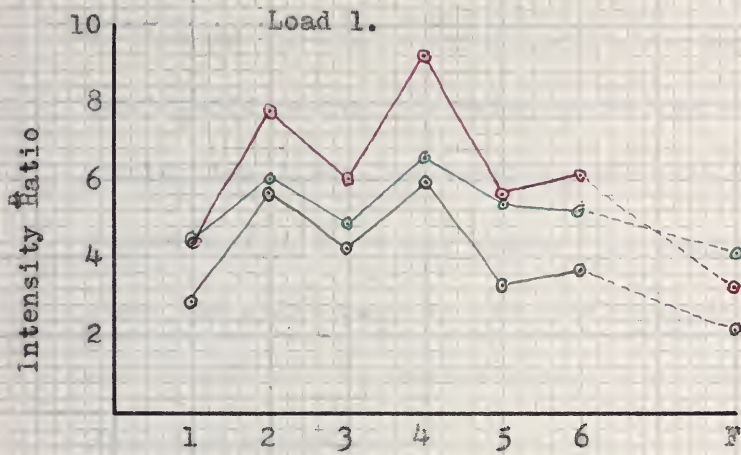
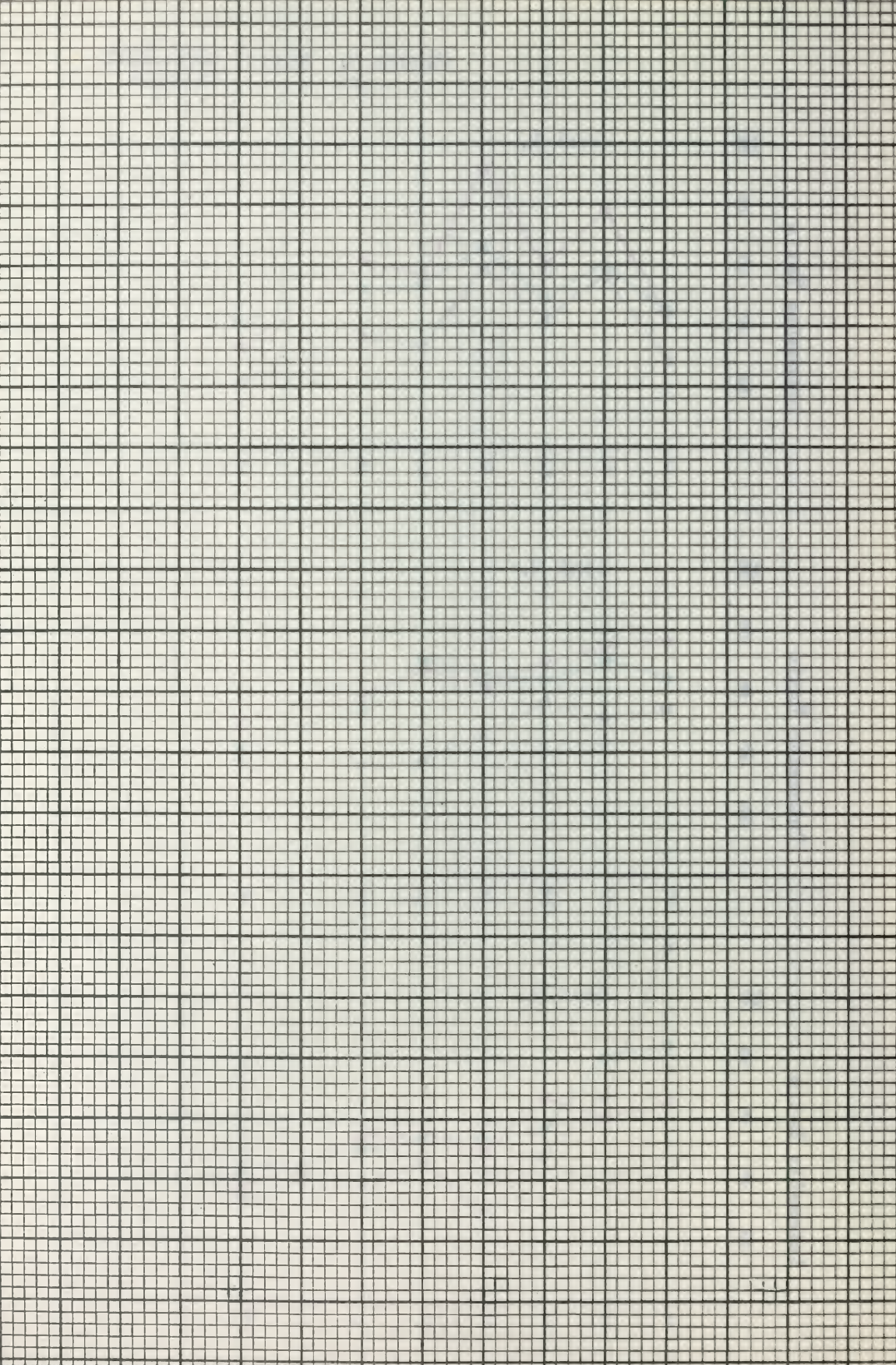


Figure 8. Ratio Call 3159
Ca 4226



Exposure in Half Oscillations



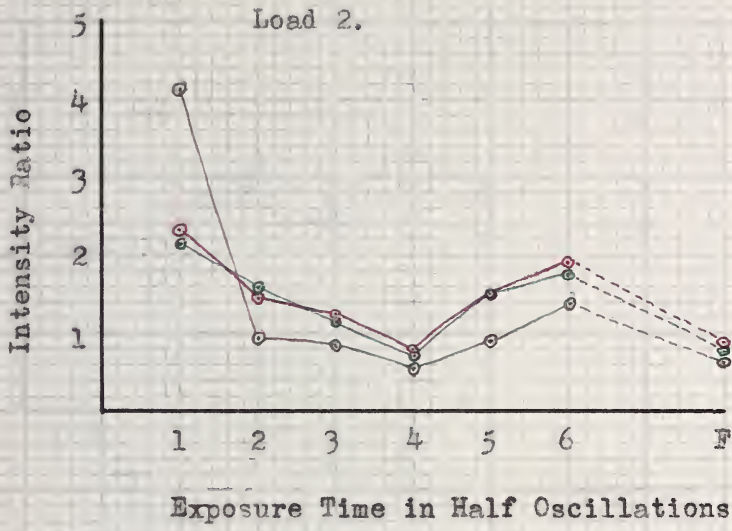
a rise on the next, and thereafter a constant value.

Boric acid caused the ratio to be low initially and climb during the first few oscillations till it reached the same value as for the other loads. In each case the temperature near the point rose in the final stages of the spark while that at the centre showed a decrease of approximately the same magnitude.

The temperature variations as measured by the behaviour of the $\text{Cd}3403/\text{Cd}3261$ ratio (Figure 7) were of the same nature as those indicated by the copper pair. The accuracy was not high enough to regard the disagreements as an indication that the excitation was not predominantly thermal. The temperature was found to be higher near the plane as before. The axial variation was greatly reduced by the addition of boric acid. This ratio could not be measured in the case of load 2 as the $\text{Cd } 3261$ line was obscured by $\text{Sn } 3262$.

The ratio $\text{Ca(II)}3159/\text{Ca}4226$ (Figure 8) shows a lower ion concentration near the plane electrode. This may be partly accounted for by a reduction in the transmission of the shutter for the 3159 \AA radiation from points near the plane due to total reflection of the E ray in the Foucaults. Complete cut-off began just below this wave-

Figure 9. Ratio $\frac{\text{SnII } 3352}{\text{Sn } 3175}$



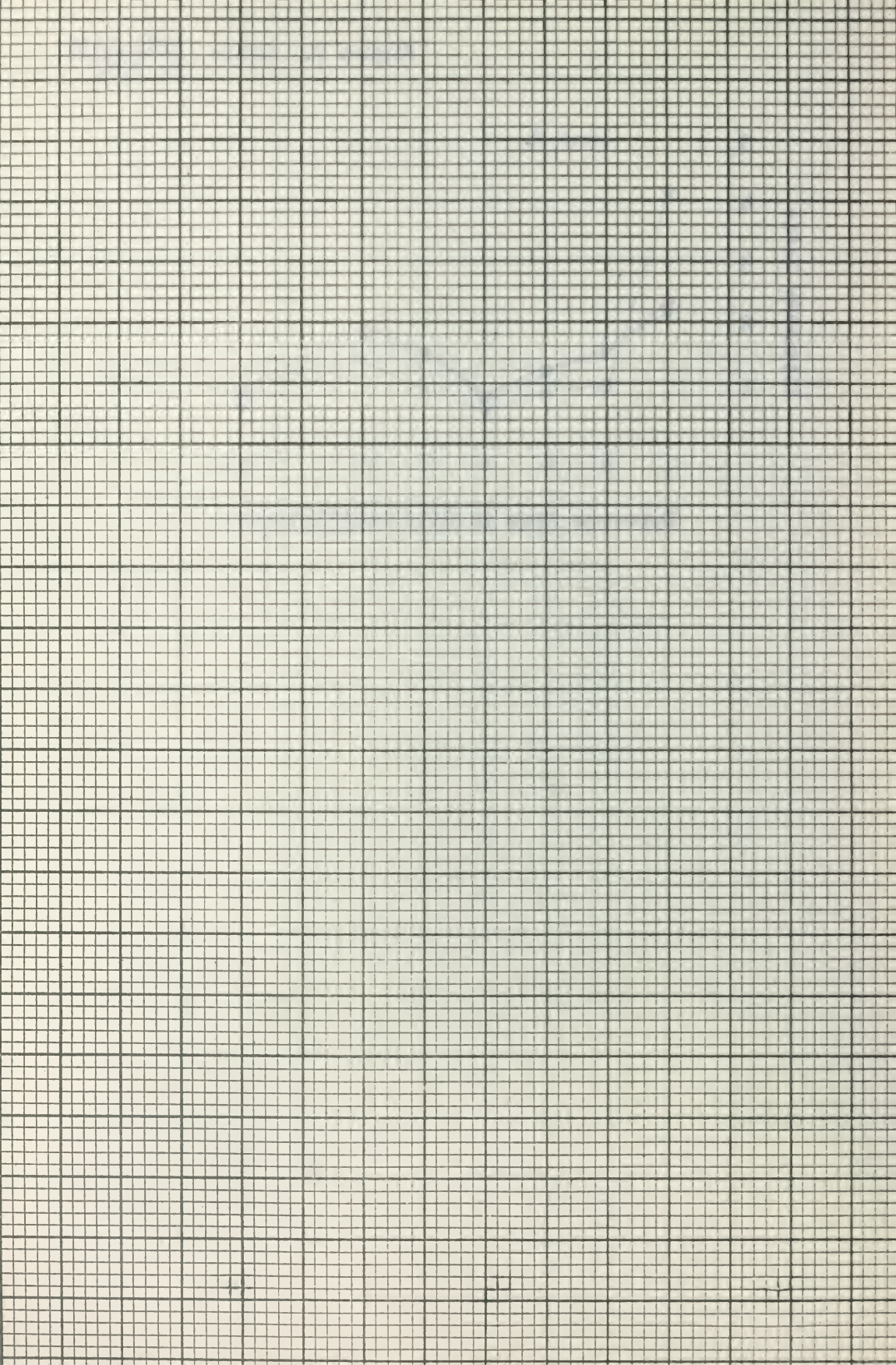
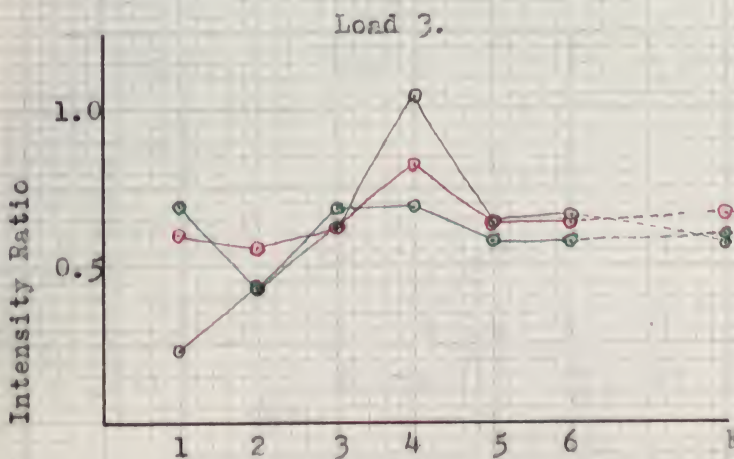
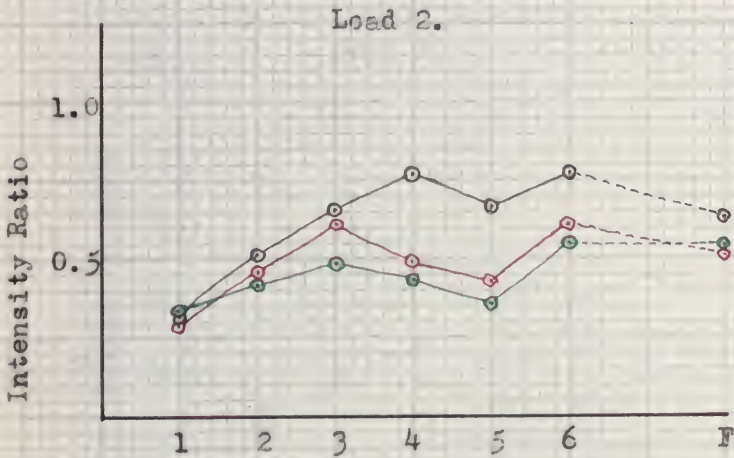
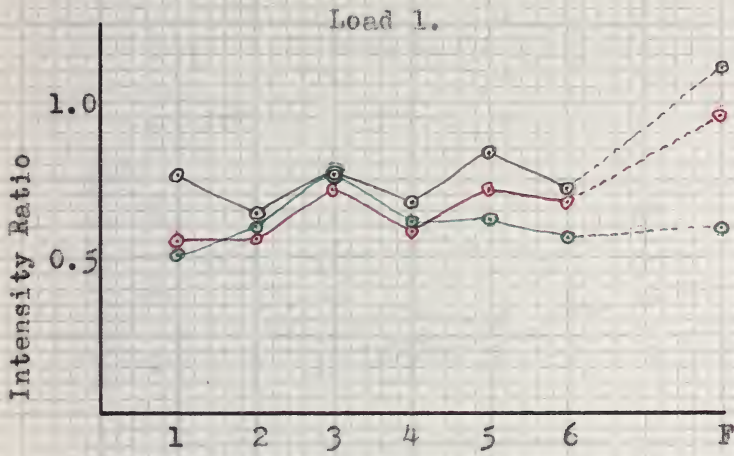


Figure 10. Ratio $\frac{Cu4226}{Cu3599(Ave)}$



Exposure Time in Half Oscillations

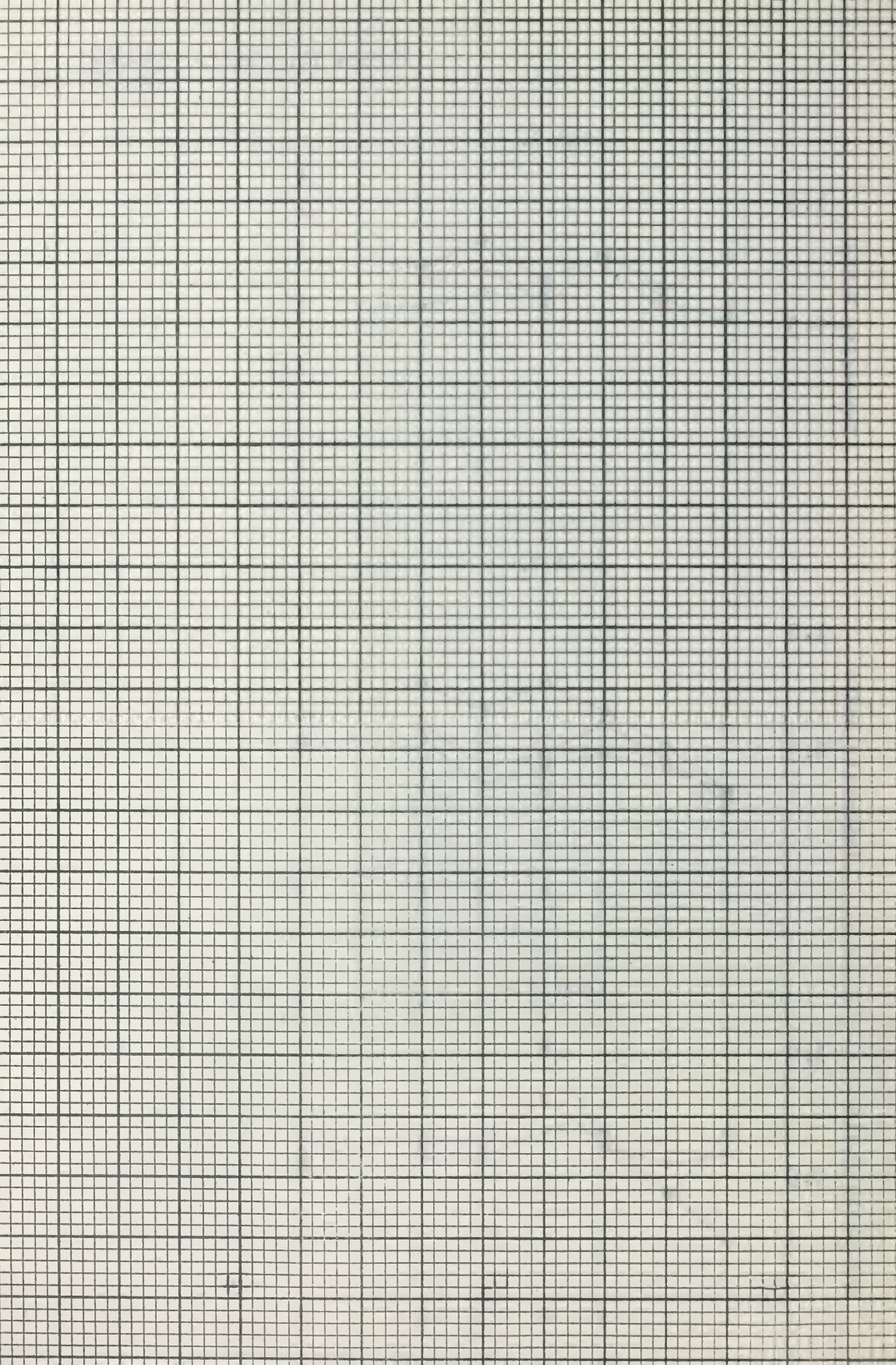
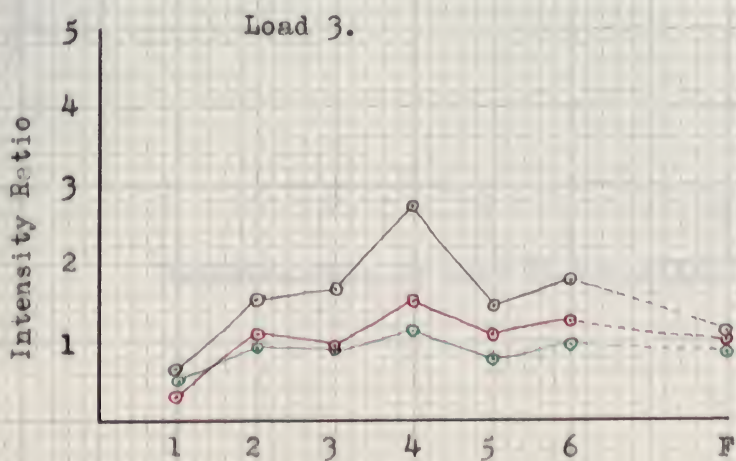
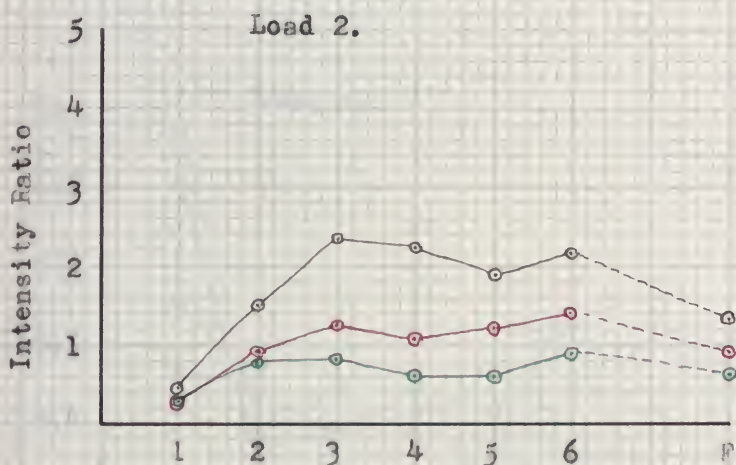
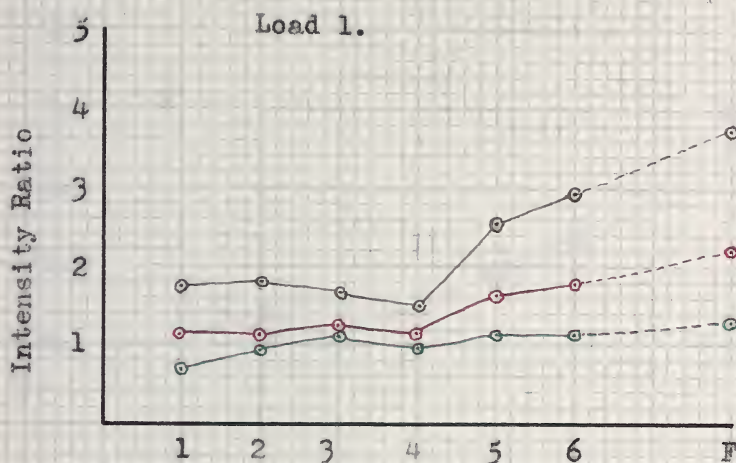


Figure 11. Ratio $\frac{Mg3838}{Cu3599}$ (Ave)



Exposure Time in Half Oscillations

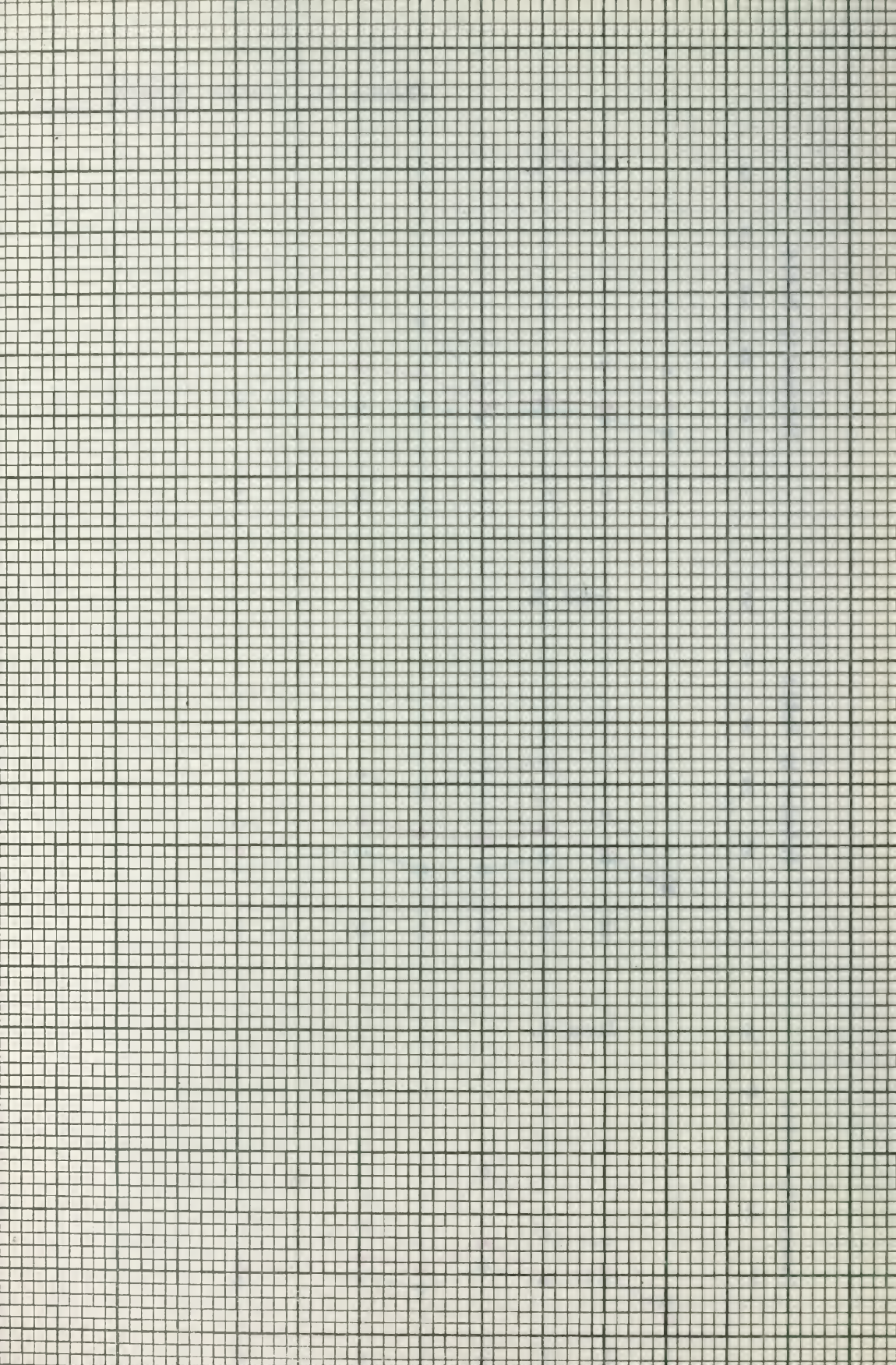
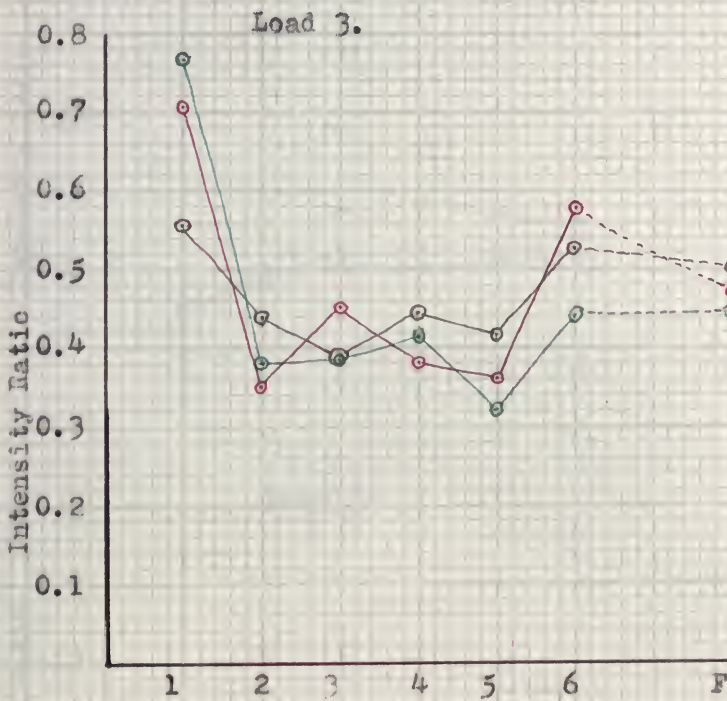
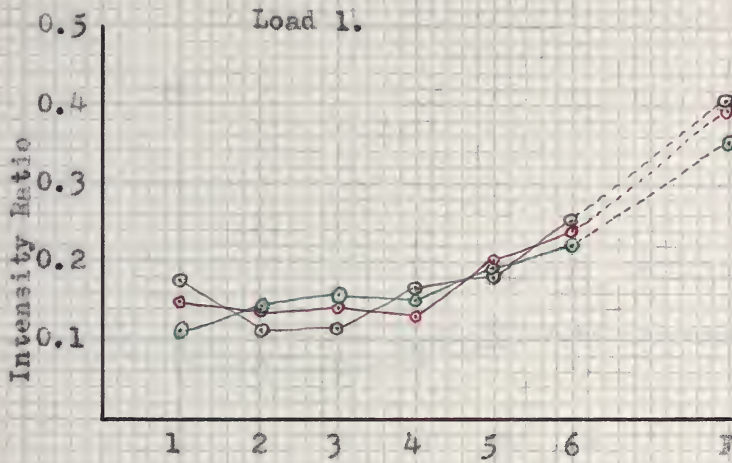


Figure 12. Ratio $\frac{\text{Cd3261}}{\text{Cu3599 (Ave)}}$



Exposure Time in Half Oscillations

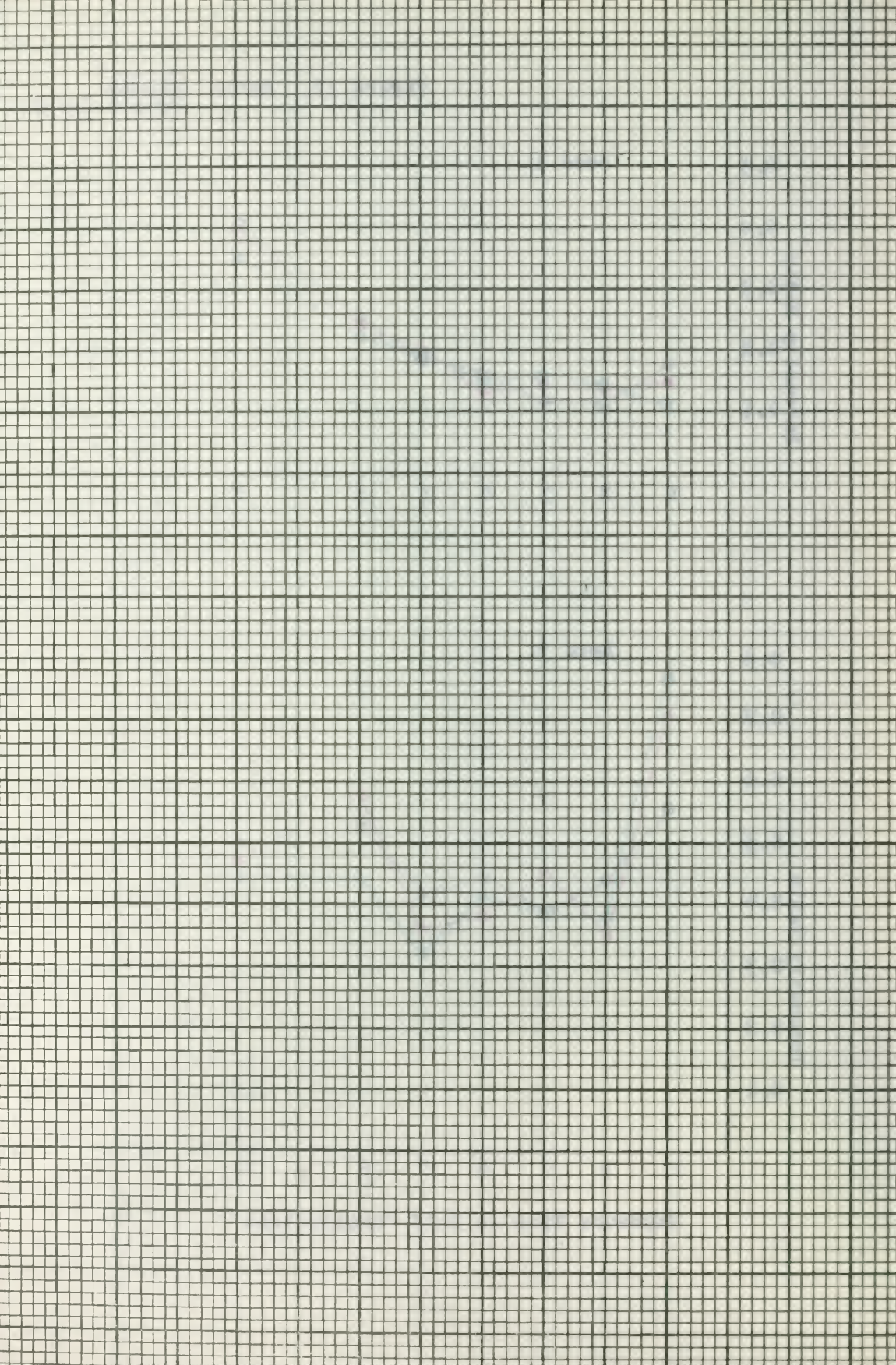
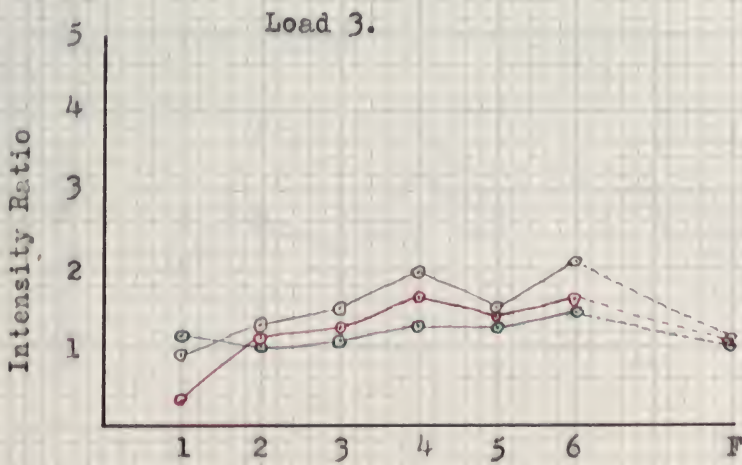
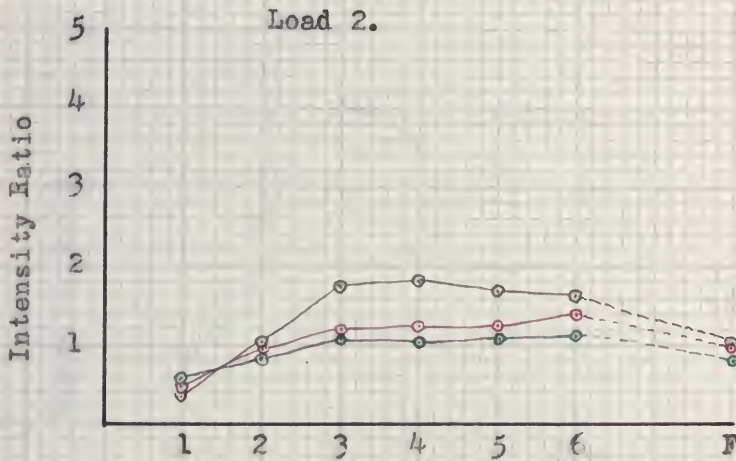
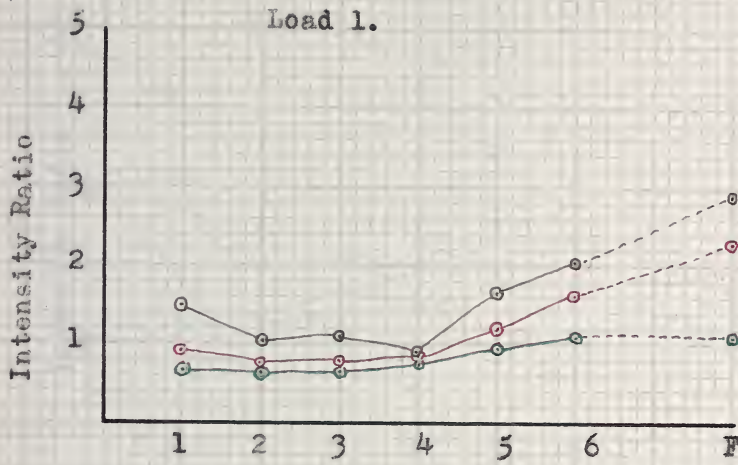


Figure 13. Ratio $\frac{\text{Cd3403}}{\text{Cu3599}}$ (Ave)



Exposure Time in Half Oscillations

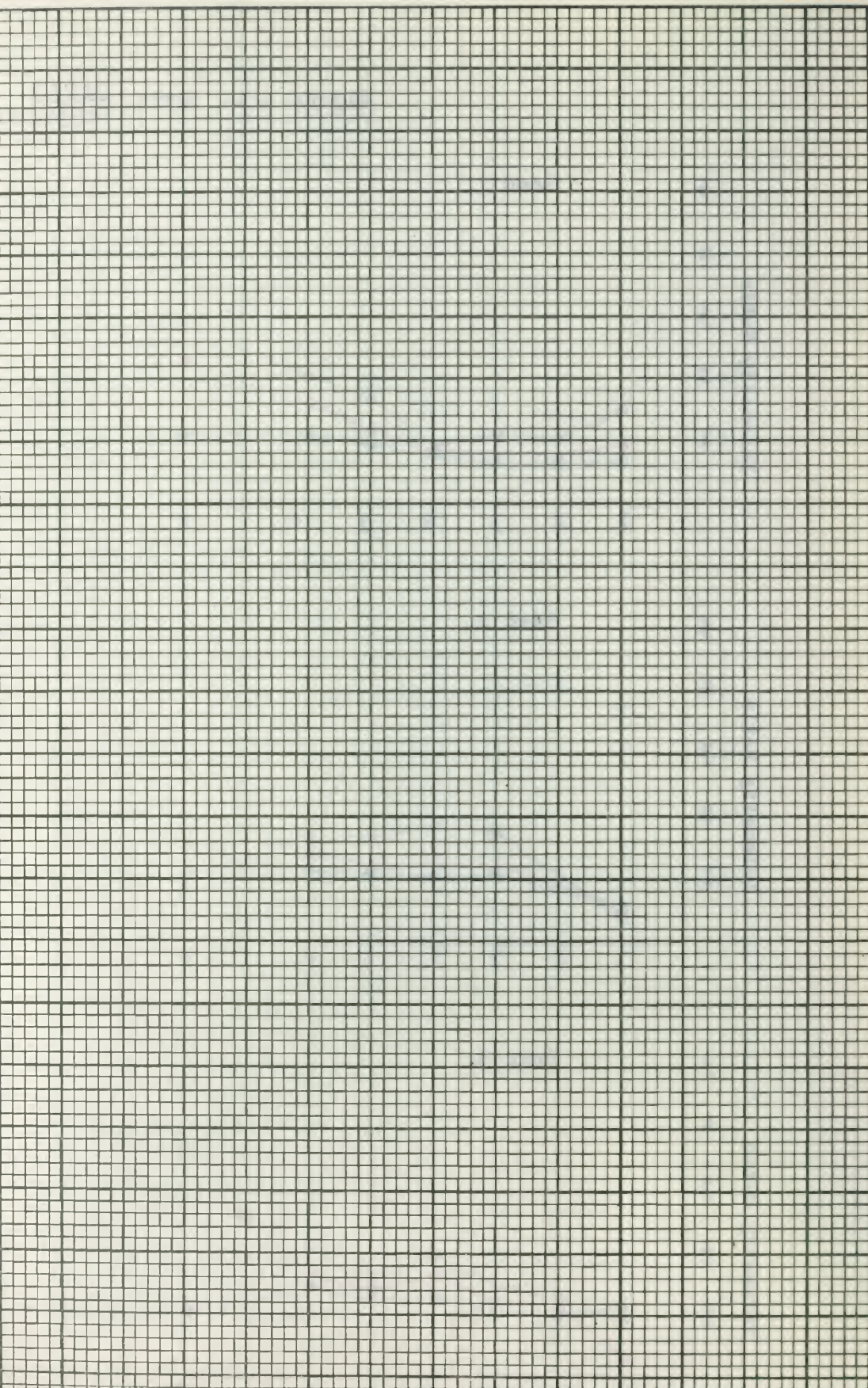
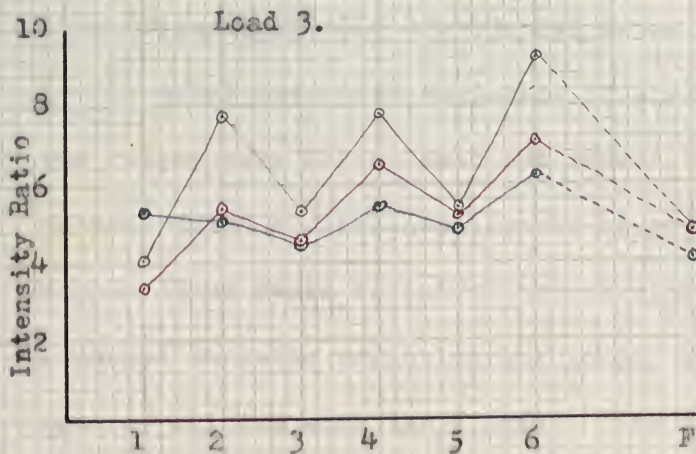
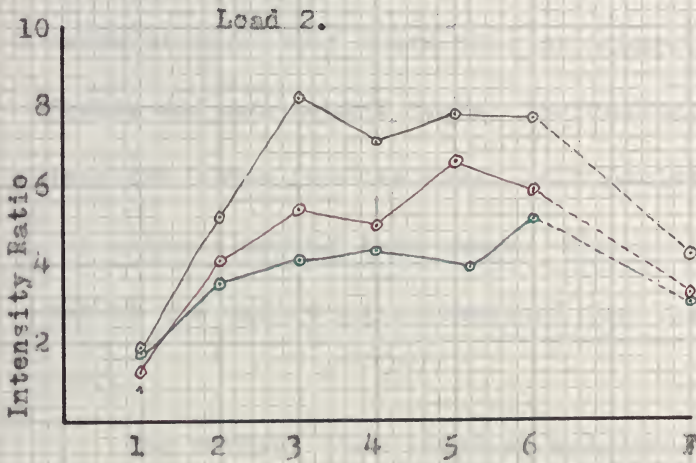
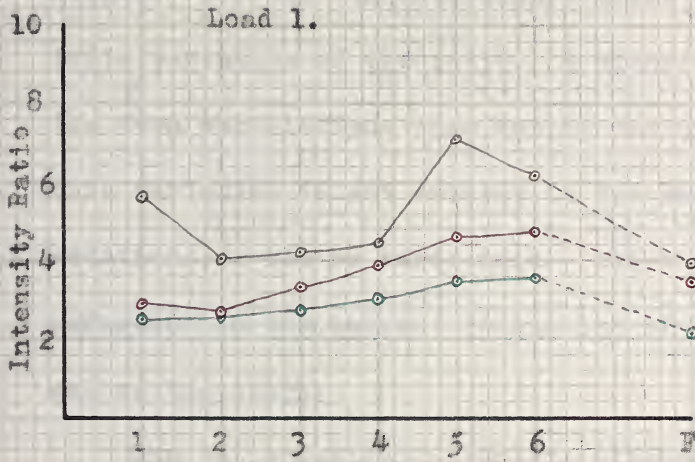
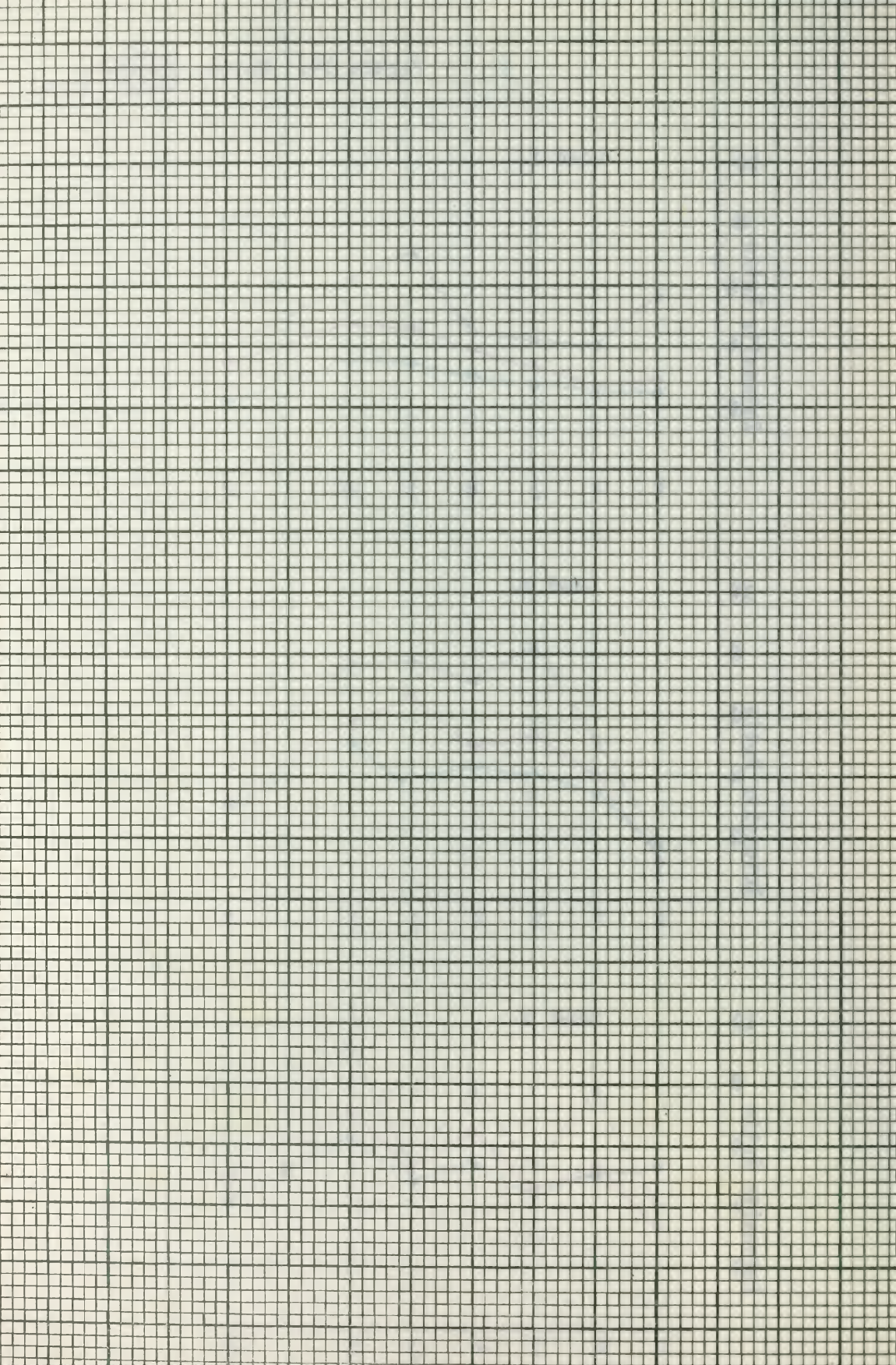


Figure 14. Ratio $\frac{Cu3610}{Cu3599}$ (Ave)



Exposure Time in Half Oscillations



length. For the standard sample there is a distinct periodic variation of the ratio. A higher temperature during the even oscillations than during the odd ones is indicated. This variation is not evident in the samples containing additions of tin or boric acid. All three show a general reduction in the percent ionization of 30-50% toward the end of the spark.

The ratio Sn(II)3352/Sn3175 (Figure 9) was high near the plane electrode for the first half oscillation after which it was lower there than at other points. Higher fields and consequent higher ionization are to be expected near the plane for the first half period as the plane is the cathode during this stage. The ratios at the point and at the centre were identical for the duration of the spark.

The neutral atom lines of calcium, magnesium, and cadmium were compared to the mean intensity of the Cu3599 line (Figures 10, 11, 12, 13, 14) so as to show more clearly the axial intensity variation in each. In all cases the ratios were higher near the loaded electrode. The concentration of load atoms would be greater there while copper atoms could be introduced at either electrode. A marked periodic variation was noted, particularly in the case of calcium with the standard load and Cd3610 with

boric acid addition. This is less evident in the other cases but may easily have been obscured by the large possible error in the intensity measurements.

The addition of boric acid caused a general reduction in the intensities of all lines as was noted by Mayhood in his measurements on the nickel and tin lines. The concentration of boron atoms in the load is fairly high so that a considerable proportion of the total radiation is from boron atoms. This results in a reduction in the numbers of other atoms released and excited.

Two of the diffuse cadmium lines end on metastable states, $^3P_2^o$ and $^3P_0^o$. The ground level is a 1S_0 term so that transitions from the two P states would necessitate a value for J of 2 or 0. The first is forbidden in any case and the second is excluded when the change is from $J=0$ to $J=0$. This introduces the possibility of self-absorption as is apt to occur in a resonance line (18) This could account for the observed reduction in the Cd3610/Cu3599 ratio in the final stages for load 1., since the concentration of cadmium atoms in the metastable state grows during the discharge. It seems reasonable to expect that the Cd 3403 line would behave in a manner similar to that of Cd3610 as the former originates at a level (3D_1) forming part of the same diffuse triplet

as the initial level (3D_3) of the Cd3610 line and also results from a transition to a metastable state ($^3P_0^o$) in the same principal triplet as the final state ($^3P_2^o$) of Cd3610. However in figure 13 the Cd3403/Cu3599 ratio shows an increase of approximately 30% in the final stages compared to the reduction of about 25% in the Cd3610/Cu3599 ratio at the same time. There are two factors that can produce a difference of this nature, assuming that the reduction is due to self-absorption. First, self-absorption varies as the third power of the wave-length, other factors being equal. This effect will produce about 18% more absorption in the 3610 A line. (18) Second, this line is two or three times as intense as the other. Consequently there will be a greater concentration of cadmium atoms in the 3P_2 state than in the 3P_0 state to cause absorption. Still, neither line is very intense, so these factors can scarcely be expected to produce such a large difference and until such a time as a more satisfactory explanation is provided, the behaviour of these lines must be considered to be anomalous.

CONCLUSIONS

The following conclusions are presented on the basis of the work outlined in this report:

1.

The region near the point electrode showed less variation than the rest of the spark, indicating that release mechanisms are more important than transport mechanisms in producing variations.

2.

A periodic variation in intensity ratios and in axial intensity distributions was evident, but more accurate and detailed measurements have to be made before any explanation of these on the basis of release, transport, and excitation phenomena can be attempted.

3.

The changes observed cannot be satisfactorily explained on the basis of changes in the effective discharge temperature alone. The ratios of neutral atom lines of copper and of cadmium indicate a higher temperature near the plane electrode on this basis. On the other hand the ratios of the ion lines to the neutral atom lines of calcium and tin show lower percentage ionization near the plane electrode.

4.

Cowan and Dieke have shown that the effects of self-absorption must be seriously considered in quantitative analysis. (18) The behaviour of the two diffuse lines of cadmium indicates that this effect may also vary over the duration of the spark.

5.

The effect of the addition of tin and boric acid as extraneous elements seemed to be to reduce the axial intensity variations near the beginning and the end of the spark and to increase them about the third to the fifth half oscillations. The samples containing tin showed smaller periodic variations than those with boric acid.

6.

The explanation of the numerous apparent anomalies requires the detailed information that can only be obtained by studying each half oscillation separately. Square-wave generators have been built for use with Kerr cell shutters in the study of the Kerr effect itself. (19) Application to this problem should not present many difficulties outside of those due to the high voltages required. Perhaps the investigation should begin with lines of higher wavelength that can be studied without the use of cell liquids that need such high fields.

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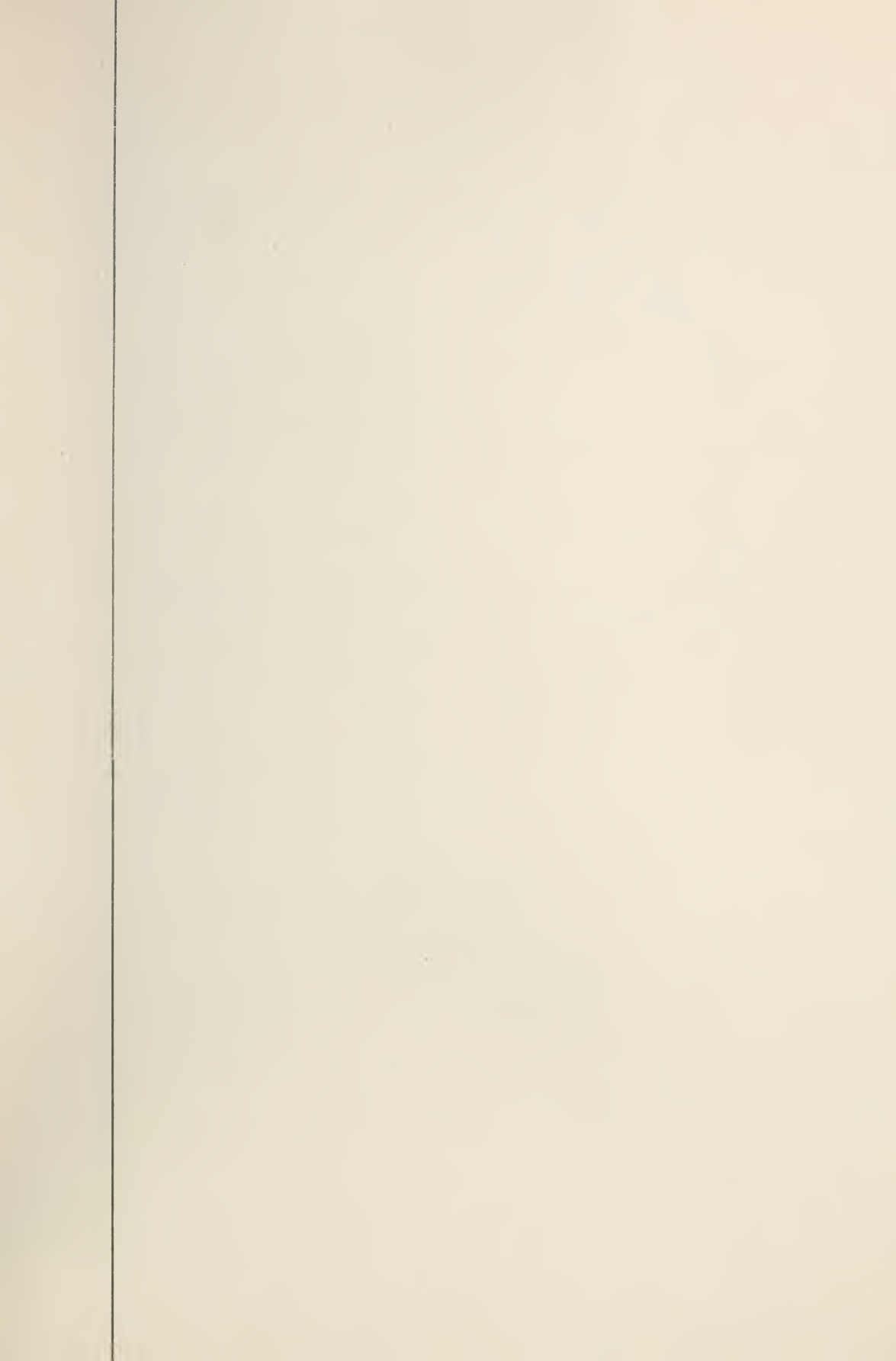
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